AD NUMBER

AD465948

NEW LIMITATION CHANGE

TO

Approved for public release, distribution unlimited

FROM

Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational Use; APR 1965. Other requests shall be referred to Air Force Flight Dynamics Lab., Wright-Patterson AFB, OH 45433.

AUTHORITY

AFFDL ltr, 6 Apr 1972

AFFDL-TR-65-12

CATALYTIC REDUCTION OF CARBON DIOXIDE TO METHANE AND WATER

G. A. REMUS, et al

GENERAL AMERICAN TRANSPORTATION CORPORATION

TECHNICAL REPORT AFFDL-TR-65-12

APRIL 1965

AIR FORCE FLIGHT DYNAMICS LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

NOTICES

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

Qualified requesters may obtain copies of this report from the Defense Documentation Center.

Foreign announcement and dissemination of this report is not authorized.

The distribution of this report is limited because the report contains technology identifiable with items on the strategic embargo lists excluded from export or re-export under U. S. Export Control Act of 1949 (63 STAT. 7) as amended (50 U. S. C. App. 2020.2031) as implemented by AFR 400-10.

Copies of this report should not be returned to the Research and Technology Division unless return is required by security considerations, contractual obligations, or notice on a specific document.

200 - June 1965 - 448-43-951

CATALYTIC REDUCTION OF CARBON DIOXIDE TO METHANE AND WATER

G. A. REMUS, et al

GENERAL AMERICAN TRANSPORTATION CORPORATION

FOREWORD

This report summarizes the work accomplished under contract AF 33(615)-1210, for research on catalytic reduction of carbon dioxide to methane and water. This work was performed under project 6146, "Atmosphere and Thermal Control", and task 614612, "Oxygen Recovery From Carbon Dioxide." The effort was initiated on 6 January 1964 and completed 31 December 1964, by the MRD Division of the General American Transportation Corporation, 7501 Natchez Avenue, Niles, Illinois 60648. The work was monitored by Lt. Derry W. Marshall, Environmental Control Branch (FDFE), Air Force Flight Dynamics Laboratory, Research and Technology Division, Wright-Patterson Air Force Base, Ohio 45433.

The work reported herein was performed by personnel within the Chemical and Biological Research Section of MRD's Environmental Systems Group, under the direction of Mr. R. A. Bambenek and supervision of Mr. J. D. Zeff. Mr. G. A. Remus served as project engineer with the assistance of Mr. R. W. Ferris for the preparation and testing of catalysts.

This report has been reviewed and is approved.

T. J. Baker
Assistant for R & T
Vehicle Equipment Division

Manuscript released by the author 15 January 1965 for publication as an RTD Technical Documentary Report.

ABSTRACT

A literature search was conducted to determine suitable candidate catalysts for the Sabatier reaction. A test system was designed and fabricated for evaluating the candidate catalysts material to select an optimum catalyst. The system included a reactor sized to handle 2.5 lbs of CO_2 per day, equivalent to one-man output. Three smaller reactors were also used to test more accurately the effects of changes in temperature, flow and catalyst configuration.

The optimum catalyst was determined to be ruthenium metal powder, having a bulk density of 85 lb/ft^3, and an average particle diameter of 0.002-0.003 inch. The minimum temperature required with this catalyst to provide over 99% conversion of CO_2 was 357°F, at one atmosphere, a H_2:CO_2 ratio of 4.4, and a space velocity of 310 hr^{-1}. During a thirty-day duration test with ruthenium metal powder CO_2 conversion remained essentially at 99%, and the catalyst remained unchanged. A short period of intermittent injection of H_2S gas into the feed gas line did not affect performance. Operation at reduced pressures down to 5 psia caused only a 1-2% decrease in CO_2 conversion with all other parameters held constant.

The theoretical equilibrium reaction limitations are discussed in the report. Various laboratory catalyst preparations and their effects on the reaction are described, and conclusion and recommendations are listed at the end of the report.

Previous page was blank, therefore not filmed.

TABLE OF CONTENTS

TABLE OF CONTENTS (cont'd)

ILLUSTRATIONS

SECTION 1

INTRODUCTION

1.1 Program Objectives

The overall objective of this program was to develop a catalyst which would efficiently promote the Sabatier process, i.e., reduction of carbon dioxide with hydrogen at low temperatures to form water and methane in high yields. Complete conversion is promoted by operating at 300°F or lower, based on theoretical equilibria with stoichiometric quantities of hydrogen and carbon dioxide. The accompanying objectives were:

1. To relate catalyst performance with catalyst properties, preparations and possible poisoning.

2. To determine yields at varying temperatures, flow rates and pressures.

3. To measure and relate power requirements for heating and initiation of the reaction with a system capable of processing 2.5 lbs. CO_2/day.

From the results of these objectives, and on the basis of a comparison of performance and operating temperatures and power requirements an optimum catalyst was to be selected.

1.2 Program Phases

The initial phase of the program consisted of a literature search of publications of work reported for the reactions between carbon dioxide and hydrogen and for all catalysts utilized in these reactions. From this search a listing of candidate catalyst materials was prepared.

The second phase consisted of the design and fabrication of an experimental system which was used to measure the catalyst perfo- ance of the selected candidate materials.

The third phase of the program was the actual testing of catalyst materials and the measurement of operating variables. In this phase data were collected on yields, temperatures, flow rates, pressures, and power requirements for the various materials tested; the effects of using different catalyst preparations were also correlated with catalyst performance. The test results from this phase were used as the basis for selection of the optimum catalyst and for the final program conclusions and recommendations.

SECTION 1

INTRODUCTION

1.1 Program Objectives

The overall objective of this program was to develop a catalyst which would efficiently promote the Sabatier process, i.e., reduction of carbon dioxide with hydrogen at low temperatures to form water and methane in high yields. Complete conversion is promoted by operating at 300°F or lower, based on theoretical equilibria with stoichiometric quantities of hydrogen and carbon dioxide. The accompanying objectives were:

1. To relate catalyst performance with catalyst properties, preparations and possible poisoning.

2. To determine yields at varying temperatures, flow rates and pressures.

3. To measure and relate power requirements for heating and initiation of the reaction with a system capable of processing 2.5 lbs. CO_2/day.

From the results of these objectives, and on the basis of a comparison of performance and operating temperatures and power requirements an optimum catalyst was to be selected.

1.2 Program Phases

The initial phase of the program consisted of a literature search of publications of work reported for the reactions between carbon dioxide and hydrogen and for all catalysts utilized in these reactions. From this search a listing of candidate catalyst materials was prepared.

The second phase consisted of the design and fabrication of an experimental system which was used to measure the catalyst performance of the selected candidate materials.

The third phase of the program was the actual testing of catalyst materials and the measurement of operating variables. In this phase data were collected on yields, temperatures, flow rates, pressures, and power requirements for the various materials tested; the effects of using different catalyst preparations were also correlated with catalyst performance. The test results from this phase were used as the basis for selection of the optimum catalyst and for the final program conclusions and recommendations.

SECTION 2

LITERATURE SEARCH

The literature search was directed mainly to investigating publications on CO_2 methanation and reduction catalysts based on independent, government and industrial research. The investigation was not limited only to reactions which give methane and water as the primary end products but also considered the general hydrogenation of carbon dioxide regardless of end products, because the catalysts used had potential application, with modification, to the Sabatier process.

2.1 Independent Research

The investigation of independent research was initiated with an extensive examination of the American Chemical Society "Chemical Abstracts". References on methanation and reduction of carbon dioxide were examined beginning with the year 1900 and extending through 1963. A large number of references, approximately seventy, were found pertinent and their abstracts recorded. Slightly over one-half of the references dealt with methane as the CO_2 reduction product, while the remainder indicated production of higher hydrocarbons, carbon monoxide, and pure carbon.

Many catalysts and combinations of catalysts were described, but those which indicated the highest methanation capability were Group VIII metals - Ru, Rh, Ir, Ni, and Co. Early work (1925) by Fischer and Tropsch showed that ruthenium will promote the reduction of CO_2 with H_2 to give only CH_4 and H_2O at 300° to 400° F and atmospheric pressure, with complete conversion of the CO_2; partial conversion starts at 200°F. Various other metals will also give complete conversion but not necessarily at as low temperatures as with ruthenium. The order of methanating activity of these metals is as shown above, according to Fischer.

Catalysts other than Group VIII pure metals promoted the formation of higher hydrocarbons such as formaldehyde. These catalysts were alloys of Group VIII metals with each other or with Cu, Ag, Au, Zn, Mn, Ba, Cr, or oxides of Al, Zn, Cr, Ba, Mn, Ti, Ce, Th, Mo, or Li.

In addition to the Chemical Abstracts, the Science Abstracts published by the Institution of Electrical Engineers and the Engineering Index published by Engineering Index, Inc., were investigated; they did not provide any data beyond that shown in the Chemical Abstracts.

2.2 Government Publications

Documents and publications from various government research and testing laboratories also were investigated in the same manner, particularly in light of the large amount of work performed in recent years in the area of catalysis by these agencies.

The literature search of government publications on contract projects, symposia, and independent reports included:

1. AEC, Nuclear Science Abstract

2. NASA, Scientific and Technical Aerospace Reports

3. NASA, Technical Publications Announcements

4. NASA, International Aerospace Abstracts

5. ASTIA, Technical Abstracts Bulletin

6. OTS, U. S. Government Research Reports.

Most of the information extracted from these sources confirmed, expanded, or refined earlier referenced work.

2.3 Industrial Publications

Publications by industrial catalyst manufacturing concerns were investigated as follows:

1. Englehard Industries, Inc., Technical Bulletin,

2. Platinum Metals Review (J. Bishop & Co.),

3. Ruthenium. The Metal, Its Alloys, Chemical Compounds and Catalytic Properties (an International Nickel Co., Inc. brochure),

4. Annotated Bibliography on Ruthenium, Rhodium, and Iridium as Catalysts (The International Nickel Co., Inc.),

5. General catalogues describing commercially available catalysts, methods of production, and equipment and procedures for evaluating catalystic parameters were obtained from Engelhard Industries, Inc., J. Bishop & Co., Nuclear Metals, Inc., Dow Metal Products Div., Dow Chemical Co., International Nickel Co., Inc., The Harshaw Chemical Co., Catalyst and Ceramic Div., Chemical Products Division of Chemetron Corp., Catalytic Combustion Corp., and Fansteel Metallurgical Corp.

6. Catalogues dealing specifically with catalyst supports and promoters were obtained from the Norton Co., Johns-Manville Celite Division, Kraft Chemical Co. (Chicago); Tamms Industries Co. (Chicago).

2.4 Summary

The literature search indicated the successful use of several materials as catalysts for carbon dioxide reduction with approximately total methanation at temperatures between 300° and 500°F. Of these materials, ruthenium provided the best performance, while other Group VIII metals also catalyzed carbon dioxide reduction.

All of the references consulted in the three areas of the literature search are tabulated in the appendix.

SECTION 3

EXPERIMENTAL SYSTEM

The experimental system was designed and fabricated to operate at a nominal capacity of 2.5 lbs. carbon dioxide/day over a test temperature range from 200° to 600°F. and at pressures of 5, 10 and 14.7 PSIA. The system was to provide the test data required to accurately monitor catalyst performance in terms of the reaction yield and temperature, at varied flow rates.

The system consists of:

1. A reactor and electric heater with variable voltage control
2. CO_2 and H_2 flow regulators and rotameters
3. A temperature sensing controller for operation of the heater
4. Manometers for reactor pressure indication
5. An outlet gas water trap and absorbent
6. An outlet gas flowmeter
7. Thermocouples and temperature indicators.

A gas chromatograph and several infra-red detectors were used to monitor the inlet and outlet gas stream composition.

Four different reactor configurations were used in the experimental system during different phases of testing. As the program progressed it became apparent that different configurations were needed because no one configuration alone provided for accurate measurement of all the testing variables.

3.1 Reactor Configuration

3.1.1 Reactor 1-G

The first reactor was fabricated from glass. This reactor was utilized prior to the design and fabrication of a full-size stainless-steel reactor for preliminary testing with commercially prepared rhodium and ruthenium catalysts. The purpose of these tests was to obtain experience with catalysts as supplied from a commercial source and to observe any performance characteristics which might affect the design or fabrication of the full-size reactor.

The 1-G reactor was made of Vycor glass, capable of withstanding 1200°F. It was 1 inch in diameter and 18 inches long. Approximately 35 grams of 1/8-inch catalyst pellets filled a 10-inch length in the tube. Two 1/8-inch diameter thermocouple wells ran through the length of the tube.

A series of preliminary tests were run with the glass tube at low CO_2

feed rates (0.2-0.3 lb. CO_2/day), and no unusual results were noted. Consequently, the full-size reactor was fabricated and incorporated into the system.

3.1.2 Reactor 1-S

The full-size reactor, designated 1-S, was made of stainless-steel and was sized to handle the carbon dioxide output of one man. This reactor was suitable for use with catalyst particles above 0.04 inch in diameter.

The design of the catalytic reactor was based on three major factors:

1. A carbon dioxide flow of 2.5 lbs/day with a stoichiometric quantity of hydrogen.

2. A catalyst bed space velocity nominally of 500/hr or higher with a catalyst bed length/diameter ratio between 3 and 4.

3. Control of the catalyst bed temperature both during start-up which requires heating, and during continuous operation which requires cooling.

Various other factors were considered, including:

1. Preheating the inlet gases to reaction temperature before the gases enter the catalyst bed,

2. Preventing outlet gases from cooling and condensing H_2O formed in the reaction,

3. Simple but multiple temperature measurements at selected points within the reactor and catalyst bed,

4. Simple removal and replacement of the catalyst material.

The reactor assembly drawing is shown in Figure 1, and a photograph in Figure 2.

Based on the required CO_2 flow, space velocity, and bed length/diameter ratio, for operation at approximately 400°F and 14.7 psia the catalyst bed dimensions are 8-inches long and 2-inches in diameter. The bed volume is 24 cubic inches and holds approximately 450 grams of 1/8-inch cylindrical alumina pellets. To provide for removing the heat of the exothermic reaction the reactor was fitted with a permanent cooling jacket, which forms an annular passage around the length of the catalyst bed. The annulus is 1/16-inch thick, and air circulates during cooling along the bed length parallel to CO_2 flow within the bed. The annulus is only 1/16-inch thick to minimuze resistance to heat transfer during start-up or subsequent bed heating. An electric heating tape, with a nominal output of 150 watts, was wrapped spirally around the outside of the jacket.

Incoming CO_2 and H_2 are heated to reaction temperature by passing centrally through the length of the catalyst within a 1/2-inch diameter tube.

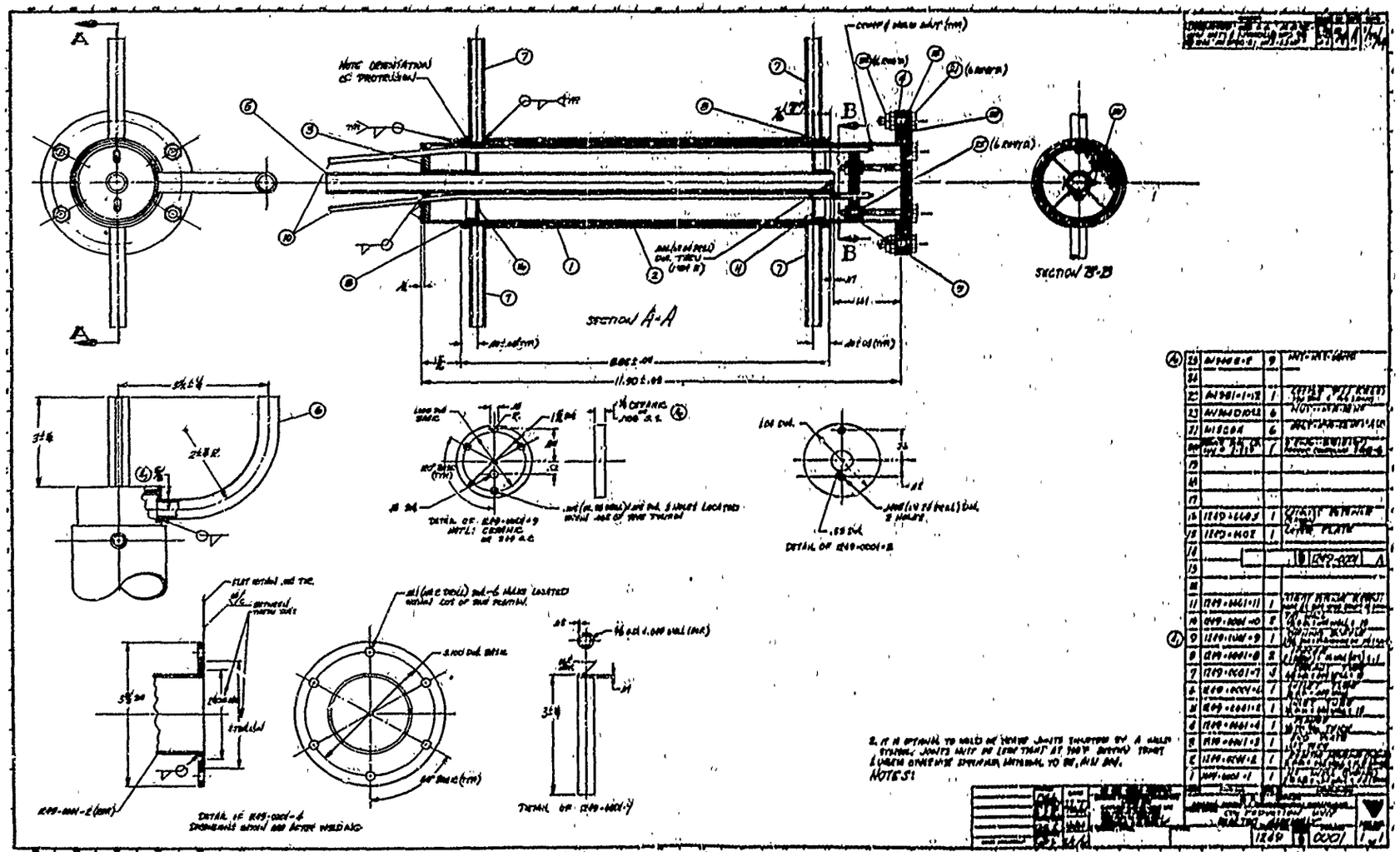

Figure 1 1-S REACTOR ASSEMBLY DRAWING

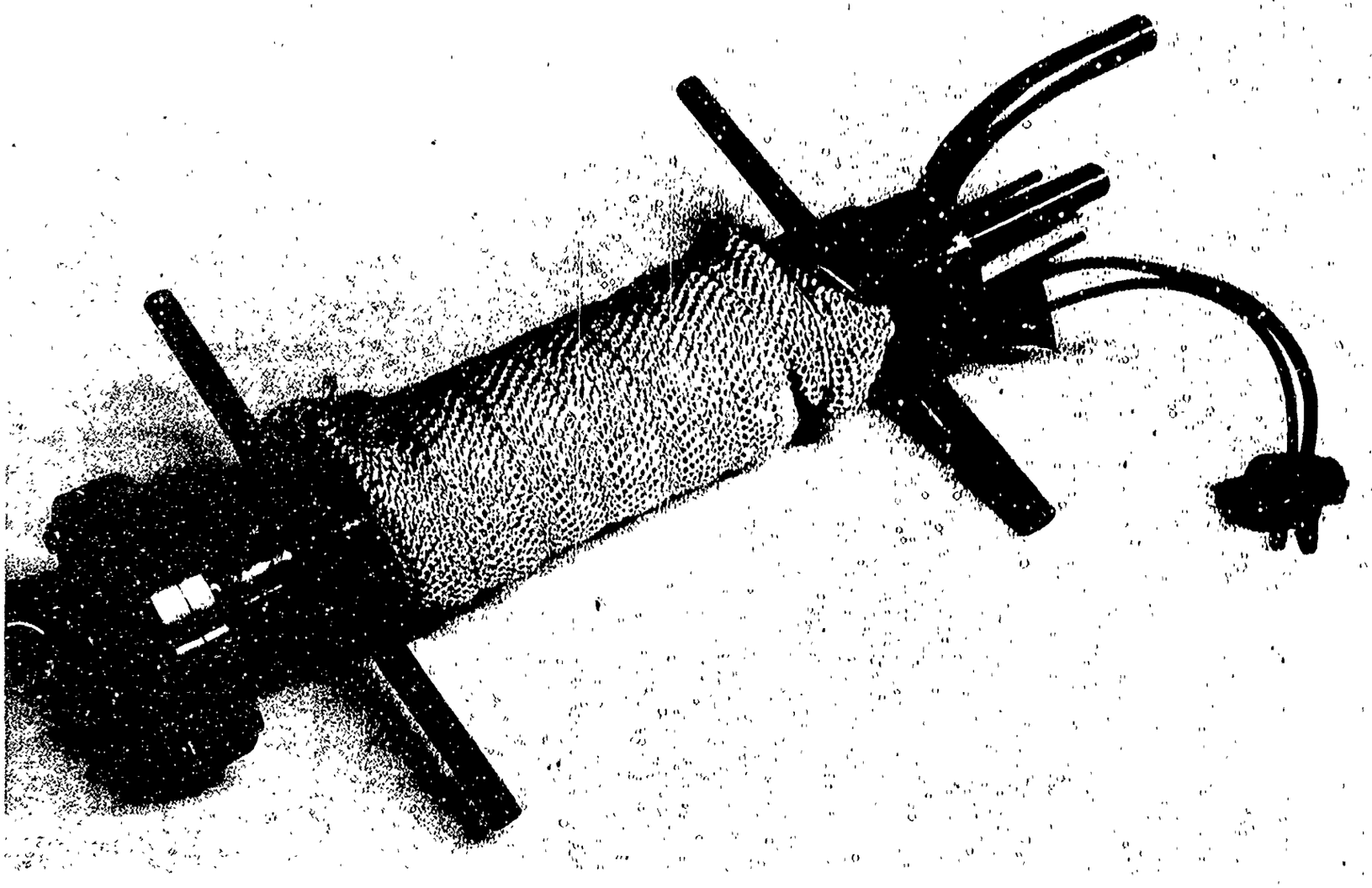

Figure 2 PHOTOGRAPH OF 1-S REACTOR ASSEMBLY

After leaving this tube the gases reverse flow direction and pass through the catalyst bed. By this means the center of the bed is cooled and the inlet gases are simultaneously preheated.

The end of the reactor where gas flow direction reverses is fitted with a flange and removable end-plate for access to the catalyst. A silicone rubber O-ring seals the end-plate to the flange. A thin metal baffle plate is attached to the inside of the end plate. This baffle prevents gas flow from striking the end-plate and traps a stationary gas volume to prevent overheating of the end-plate and possible damage to the O-ring seal.

At the opposite end of the reactor a 1/2-inch diameter outlet tube discharges from the wall of the reactor. Hot reaction gases contact all surfaces of this end to maintain a high temperature and prevent H_2O condensation.

The catalyst is contained between two removable perforated disks which slip over and are supported on the central gas inlet tube. Two temperature wells of 1/8-inch diameter are located in the catalyst along the length of (1) the gas inlet tube, and (2) the inner surface of the reactor wall. Temperatures are measured at various points in the well by moveable thermocouples. The reactor was fabricated entirely from stainless-steel; all seams were heliarc welded, except for the thermocouple well connections which were brazed.

This reactor configuration provided data on gas flow rates, power inputs, and temperature control techniques. However, during operation, a 100°-250°F temperature gradient in both the axial and radial direction of the catalyst bed prevented accurate measurement of the reaction temperature.

3.1.3 Reactor 2-G

Primarily to eliminate the extreme temperature gradient problem, a second glass reactor was fabricated, and designated No. 2-G. The reactor, shown in Figure 3, provides the following:

1. A catalyst support for fine catalyst metal powders, and catalysts on fine support powders, up to 150 mesh;

2. A smaller catalyst bed volume which permits testing smaller amounts of catalysts, and which minimizes the temperature gradients in the bed.

This reactor differed from the original glass reactor (1-G) in that its length to diameter ratio was approximately 2:1 instead of 10:1, although the total catalyst bed volumes were approximately the same. The 2-G reactor was heated externally by a spirally wrapped heating coil. No provision was made for cooling the reactor because it was anticipated that radiation and convection away from the outer reactor surfaces would provide adequate heat removal.

Two thermocouple wells, one at the bed wall and the other at the bed center, were used to measure temperatures within the catalyst. Inlet gases were not preheated.

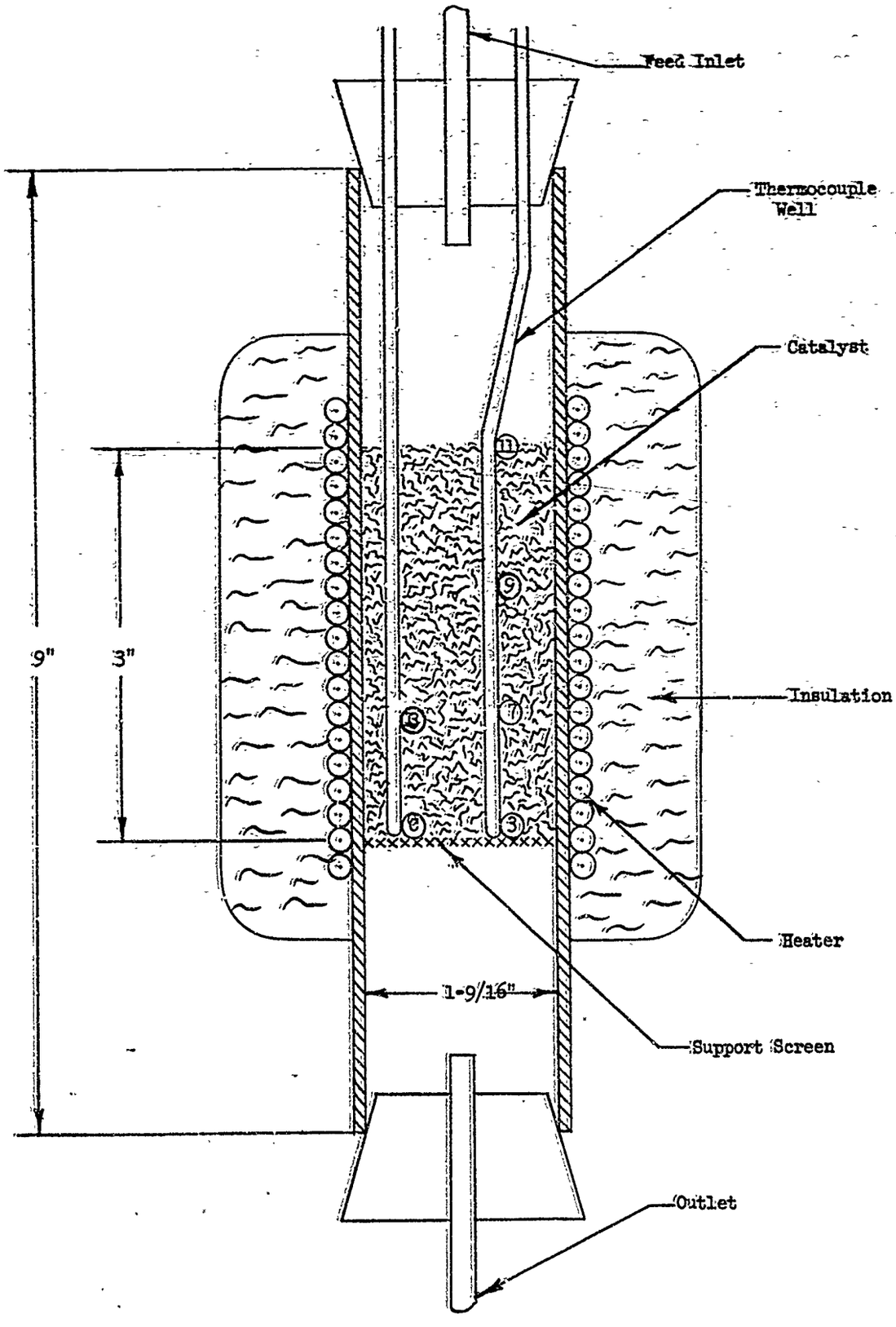

Figure 3 2-G REACTOR SCHEMATIC DRAWING

Although operations with this reactor essentially eliminated excessive temperature gradients in the catalyst bed, and permitted testing of catalyst powders, the reactor volume was large and did not provide for testing of low volumes, in the range of 10 cc, of catalyst materials.

3.1.4 Reactor 3-G

In order that tests could be performed on limited amounts of catalyst, a third glass reactor (designated 3-G) was fabricated. This reactor is shown in Figure 4.

This reactor was designed primarily for testing pure metals in the platinum family which are generally available only in powder form, approximately 150- to 200-mesh (0.003 to 0.002-inch average particle diameter). Flow in this reactor is upward, since preliminary tests showed downward flow through powder of this mesh size creates a very high (3-4 psi) pressure drop through a 1- to 2-inch deep layer. The top of the reactor is curved into an elbow and heated to prevent condensation of product water which could otherwise condense and collect on the catalyst surface and impair the reaction.

3.2 Test Monitoring and Control System

The test monitoring and control system consisted of the following components as shown in Figure 5:

1. CO_2 and H_2 flow regulators and rotameters
2. A temperature sensing controller for heater operation
3. A water manometer for inlet reactor pressure indication
4. An outlet gas flowmeter
5. Thermocouples and temperature indicators
6. Gas analyzers for measuring feed and outlet gas compositions

The CO_2 and H_2 flow regulators were 1/4-inch Nuclear Products Company vernier fine metering valves, fed by Bastian and Blessing low pressure single-stage regulators set at 2 psig. The rotometers were Fischer and Porter 2SA-19202 glass flowmeters with sapphire floats, with a nominal maximum capacity of 960 cc/min based on standard air. The temperature controller was a West Instrument Corp. Model J indicating pyrometric controller actuated by a thermocouple sensing the catalyst bed temperature. The outlet gas flowmeter was an American Meter Company Model No. AL-17-1 Wet Test Meter, having a maximum flow rate capacity of 4.7 liters/hr. The thermocouple used was Chromel-Alumel, and the temperature indicator-recorder was a Minneapolis Honeywell 24-point multipoint recorder.

A Beckman GC-2 chromatograph with a thermal conductivity detector was used initially to monitor the inlet and outlet gas stream. The changes in composition were fairly rapid and the chromatograph response time was inadequate for closely relating degree of conversion to temperature.

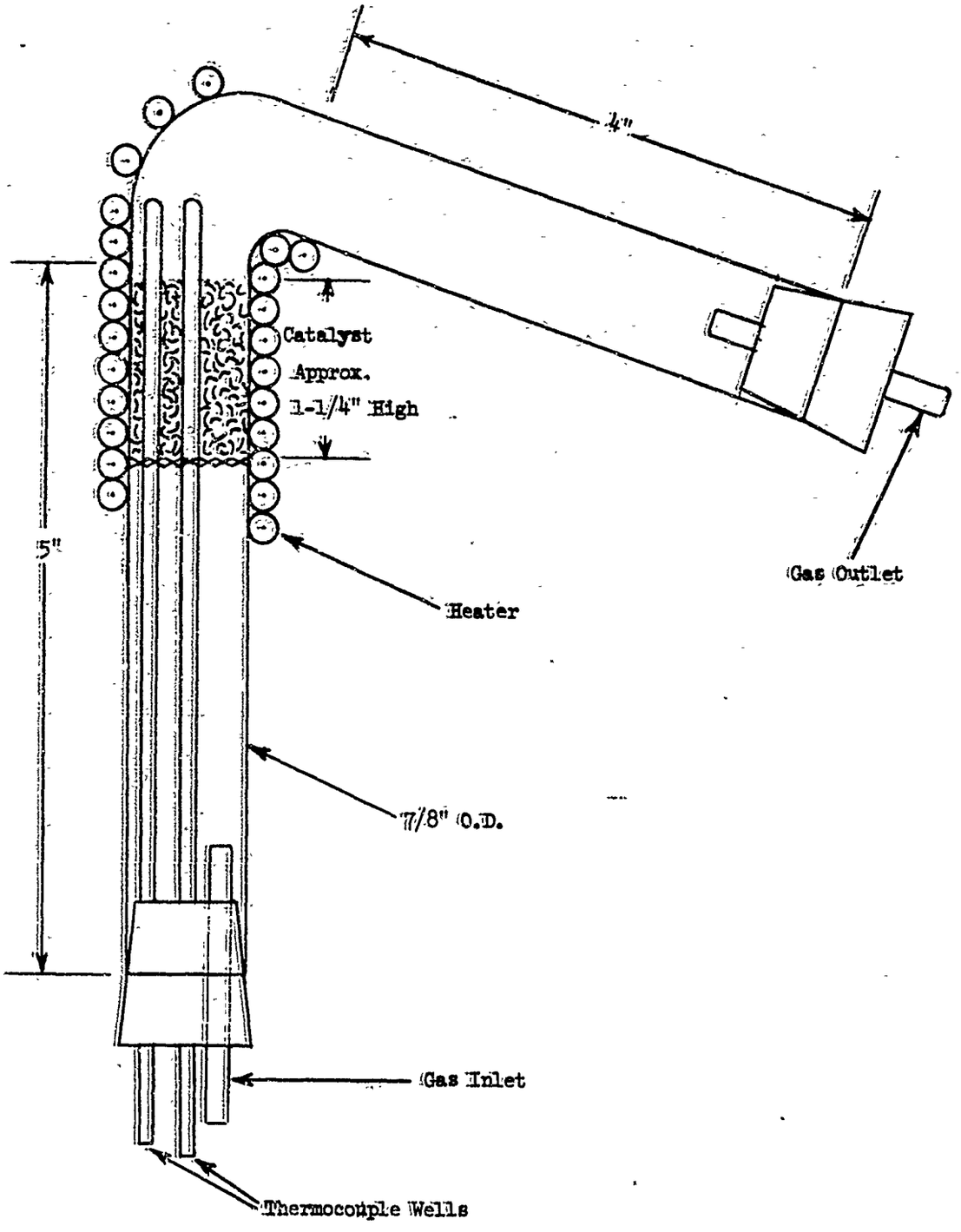

Figure 4 3-G REACTOR SCHEMATIC DRAWING

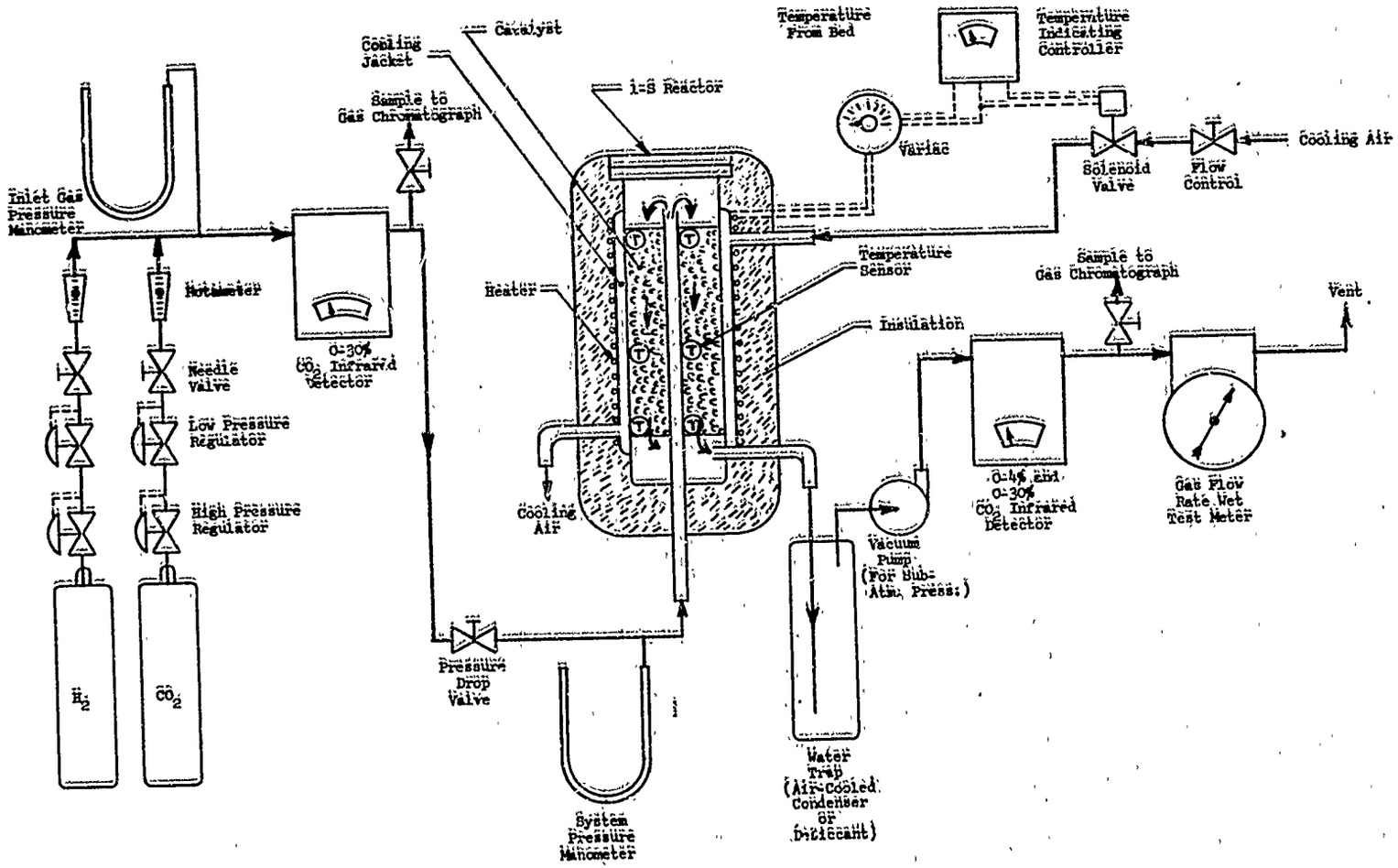

Figure 5 EXPERIMENTAL TEST SYSTEM WITH 1-S REACTOR

Subsequently, the chromatograph was replaced by two Mine Safety Appliance Co. LIRA Model 300 Infra-red detectors both reading 0-30% CO_2 by volume. The detectors continually and separately monitored the inlet and outlet gas composition. The signal from the outlet detector was fed into a series of points on the 24-point recorder to give a relatively continuous indication of degree of CO_2 conversion simultaneously with temperature indication.

SECTION 4

CATALYST TESTING PROGRAM

The catalyst testing program was concerned with the actual performance rating of a series of catalysts tested under varied operating conditions. The primary objective was to determine the optimum catalyst which would provide essentially complete (99% or higher) CO_2 conversion at the lowest temperature. The accompanying major objectives were to relate catalyst performance with catalyst properties and preparations, and to determine temperature, pressure, and space velocity effects on CO_2 conversion. During testing the power and cooling necessary for initiation and control of the reaction were measured for a system operating at one-man capacity.

4.1 General Plan

The overall approach for catalyst testing considered several basic factors. First, the theoretical aspects of the chemical reaction were examined to determine temperature and pressure limitations, where possible, based on chemical equilibrium theory. The theoretical calculations indicated the practical temperature ranges and the effects of subatmospheric pressures for actual experimental testing.

Second, candidate catalyst materials were procured specifically as catalysts from industrial manufacturers, to take advantage of the specific properties designed into the materials by the manufacturers. The physical properties of these catalysts, such as size, density, shape, chemical composition, support material, etc., were used as the basis for final selection for actual testing.

Third, based on the performance of industrial catalysts, laboratory preparations were made of high performance catalyst materials to show the effects of preparations on the amount of CO_2 converted. Also, various industrial catalyst materials were pre-treated in the laboratory to determine the effects of pre-treatments such as hydrogen reduction, air oxidation, or surface activation with mineral acids.

Finally, both the industrial and the laboratory-prepared catalyst materials were tested under varied conditions of temperature, flow, feed composition, and pressure. These parameters were varied to provide sufficient data to adequately rate the performance of each material, to determine the minimum operating reaction temperature, and to ultimately determine the overall optimum catalyst along with the power and cooling requirements for sustained, controlled and efficient reactor operation.

4.2 Reaction Theory

The chemical equation for the Sabatier reaction is:

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O$$

The equilibrium relation is:

$$K_p = \frac{[CH_4][H_2O]^2}{[CO_2][H_2]^4\pi^2}$$

where K_p = Equilibrium constant, pressure

$[\ ]$ = Volume concentration = Mole fraction

π = Total pressure

If the degree of conversion of CO_2 is represented by X, then the number of moles of CO_2 at equilibrium is $1 - X$, of H_2 is $4 - 4X$, of CH_4 is X, of H_2O is 2X, and the total present is $5 - 2X$.

The equilibrium relation becomes:

$$K_p = \frac{(X)(2X)^2(5-2X)^5}{(1-X)(4-4X)^4(5-2X)^3\pi^2} = \frac{X^3(5-2X)^2}{64(1-X)^5\pi^2}$$

From the Gibbs' free energy relationship, enthalpies, and standard heats of formation the equilibrium constant may be related to temperatures to give the graph shown in Figure 6.

From the equilibrium equation and this graph, the theoretical degree of CO_2 conversion can be related directly to the equilibrium temperature. This relationship is depicted in Figure 7 which shows the maximum possible CO_2 conversion at atmospheric pressure and any given temperature for a stoichiometric H_2:CO_2 ratio of 4:1.

From this curve it can be seen that, from equilibrium considerations, it is desirable to operate the reaction at temperatures approximating 300°F for 100% CO_2 conversion, or up to 400°F for 99% conversion; operation at temperatures higher than these will prohibit this high degree of CO_2 conversion.

If all of the reactor bed were at a temperature higher than 400°F, it would be impossible to achieve 99% conversion, with the actual possible degree conversion governed by the minimum temperatures in the bed. In practice, however, there is usually a temperature gradient in the bed, with the inlet running higher than the outlet.

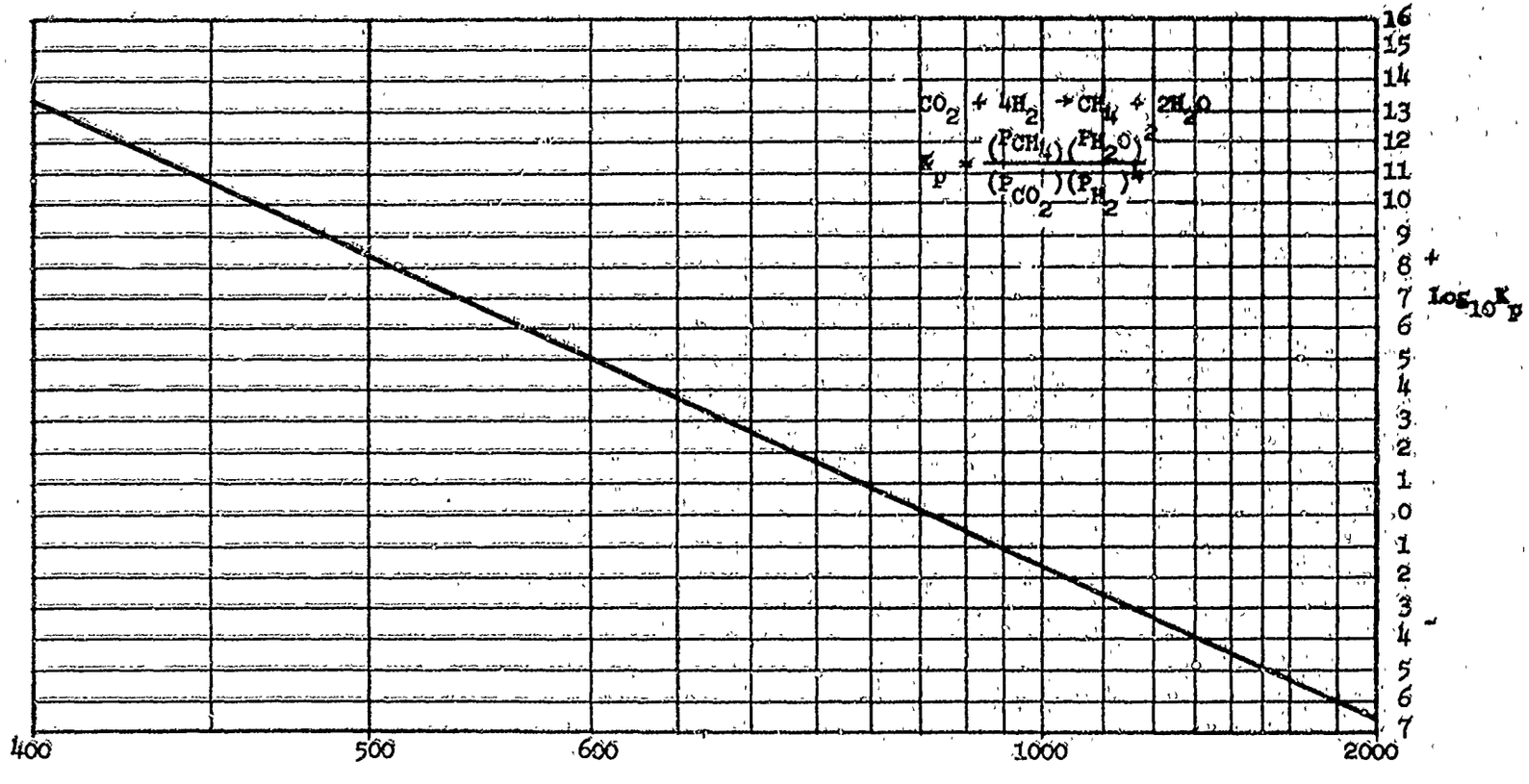

Figure 6 EQUILIBRIUM CONSTANT VS. TEMPERATURE

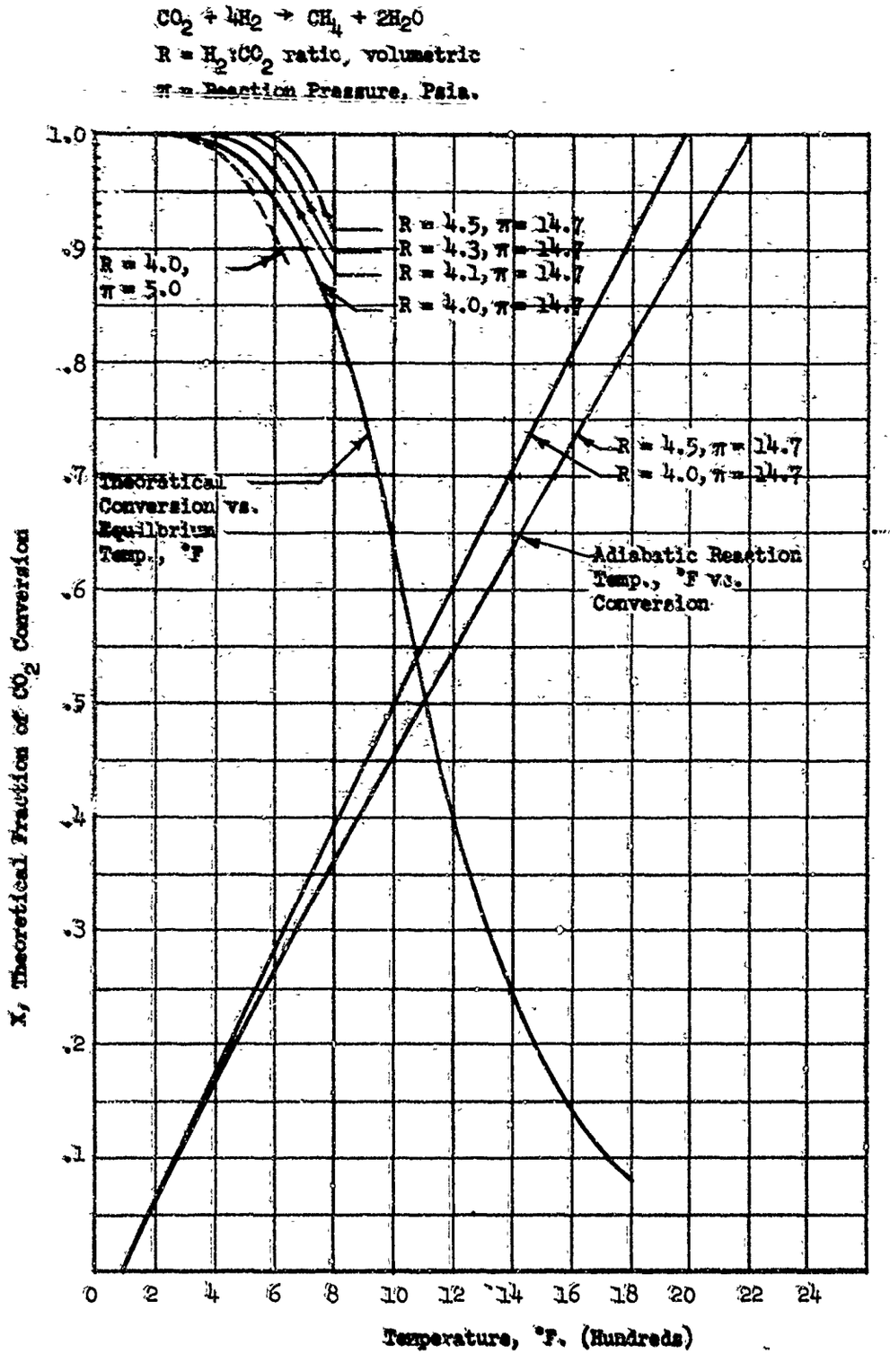

Figure 7 THEORETICAL CO_2 EQUILIBRIUM CONVERSION VS. TEMPERATURE

For example, at the inlet where the temperature may be 550°F, due to the exothermic energy release, conversion will approximate 96%, while the middle is at 400°F with 99% conversion, and the outlet at 300°F, with conversion approaching 100%.

Complete conversion would thus be achieved but only because a sufficient portion of the reactor was at 300°F. The ideal theoretical reactor would operate isothermally at a maximum of 300°F, with the inlet gases preheated to this temperature level. If the reaction could be initiated and sustained at even lower temperatures complete conversion would still be achieved. This lower temperature would be limited only by the vapor pressure and corresponding dew point of the product water. Condensation of product water within the catalyst bed could have the undesirable effect of decreasing the activity and capacity of the reactor.

The theoretical temperature to which the gas mixture could rise in an adiabatic reaction may be calculated from the standard heat of reaction, the heat capacities of the reactants and products, and the degree of CO_2 conversion. By using mean molal heat capacities the temperature may be closely approximated by the following equation:

$$T = T_{Ref.} + (\Delta H_R)(X)/(XC_1 + 2XC_2 + (1 - X)\ C_3 + 4\ (1 - X)\ C_4$$

where T = theoretical reaction temperature

$T_{Ref.}$ = standard reference temperature, 77°F (25°C)

ΔH_R = standard heat of reaction

X = degree of CO_2 conversion

C = mean molal heat capacity between T and $T_{Ref.}$ with subscripts 1 = CH_4, 2 = H_2O, 3 = CO_2, and 4 = H_2

Curves of the temperature versus CO_2 conversion are shown also on Figure 7, for H_2:CO_2 ratios of 4.0 and 4.5. (For H_2:CO_2 = 4.5 the coefficient of $(1 - X)C_4$ becomes 4.5).

The intersection of this curve with the equilibrium conversion curve indicates the maximum temperature to which the reactor bed could rise in an uncooled reactor.

As can be seen from the graph, the temperature would approximate 1080°F, and conversion would be 50%. This temperature is of importance in reactor design since it demonstrates the maximum to which reactor materials would be subjected in an emergency operation where cooling failed.

For operation with the $H_2:CO_2$ ratio greater than 4.0 the family of short curves aligned with the equilibrium curve shows the effect of these ratios with values of 4.1, 4.3 and 4.5. At a ratio of 4.5 a conversion of 99% is possible at temperatures up to approximately 575°F, as compared to 400°F for a 4.0 ratio. These curves thus demonstrate that 99-100% conversions are possible well above the 400°F limit if the $H_2:CO_2$ ratio is increased by only a slight amount.

The effects of operating at pressures below atmospheric can also be determined theoretically from the equilibrium relation, by substituting appropriate values for π in the equilibrium equation. The dotted line on Figure 7 shows the maximum possible CO_2 conversion versus temperature for stoichiometric-$H_2:CO_2$ ratio of 4:1, but at 5 psia.

From the dotted curve it can be seen that the maximum temperature for 99% conversion at this pressure is approximately 360°F, which is 40°F below the maximum at atmospheric pressure. The curve shows that the effect of operating at lower pressures may be offset if the reaction can be catalyzed to completion at a lower temperature. This again is due to the fact that the equilibrium constant increases with decreasing temperature.

In summary, the effect of operating at subatmospheric pressures down to 5 psia should be negligible from equilibrium considerations in a reaction temperature range of 300° to 400°F.

The effects of changing the space velocity through the reactor could not be predicted with reliability, since these effects are dependent on the kinetics of the reaction. The theoretical kinetic aspects of the reaction are such that estimates of the reaction rate could be in error by one or two orders of magnitude, based on the present state of kinetic theory.

In practice the space velocity through the reactor was held in the range of 500/hr, based on the conclusions in Technical Documentary Report No. FDL 64-22, Part I, "Investigation of Catalytic Reactions for CO_2 Reduction," E. B. Thompson, Jr., October 1964.

4.3 Experimental Test Results

In this section the experimental results are discussed for all of the catalysts tested in each of the different reactors. Summaries of all tests in the complete program are listed consecutively in numerical order and are shown in the appendix.

Also in this section the commercial catalysts used are described along with support materials. The results of the tests are summarized in terms of catalyst performance, and the effects of various catalyst preparations, temperature, pressure, and space velocity are related to overall performance. Following the discussion of the test results the details of the chemical preparations are summarized for each of the catalysts prepared in the MRD laboratories.

Based on CO_2 conversion, sustained operation, minimum temperature, and power and cooling requirements the optimum catalyst was selected.

4.3.1 Catalyst and Support Materials

The materials tested in this program as potential catalyst candidates were selected from a listing based on the literature search. The list of candidate materials was:

Ru, Rh, Ir, Ni, Co, Os, Pt, Pd, Ta, W, Cb, Mo.

These materials were procured primarily from catalyst manufacturers but also from manufacturers of the pure metals or metal oxides. The materials procured specifically as catalysts were supported on various media, namely, alumina (Al_2O_3), carbon, and kieselguhr (diatomaceous earth). These support media were in the form of either 1/8 x 1/8 and 3/16 x 3/16-inch cylinders, or powders between 150 and 250 mesh.

All of the candidate materials except tungsten and tantalum were procured specifically as catalysts and supplied on one or more of these support media. Most of the materials were also procured as pure metals in powder form ranging in size from 80 to 250 mesh. The table in Figure 8 shows a listing of the candidate materials and supports tested and the associated experiment number(s) for each material.

For initial testing in the program, commercial catalysts were selected instead of laboratory prepared catalysts, to take advantage of the specific catalytic properties designed into the catalyst and support by the commercial manufacturers. In this manner the experience and preparative techniques of these manufacturers were utilized, and the likelihood of successful reactor operation was increased.

Pelleted catalysts were used because they provided a high surface area for a given weight of catalytic agent. This was of importance in testing metals in the platinum family. Also the pelleted catalysts were easily and readily tested in the full-size reactor while powdered materials were not, since the powders could pass through the perforated disks on the ends of the catalyst bed.

The pelleted alumina-supported catalysts in the platinum family were 0.5% metal by weight on Al_2O_3. Physical examination of this pellet showed the metals impregnated to depths between .01 and .03 inches into the surface of the alumina, rather than as a very thin pure metallic layer on the outer pellet surface. Nickel and its oxide and amine derivatives in pelleted form, both on alumina and kieselguhr supports, were homogeneous pellets with no distinctive outer surface layer. The amount of nickel in the pellets ranged from 10% to 60% by weight.

Although the supported catalysts were metallic in nature, they were not electrically conductive, indicating that the metals were combined with the supports in other than a purely mechanical fashion. The support materials were activated alumina, pure carbon, and kieselguhr. Kieselguhr is essentially a hydrous amorphous silica containing trace amounts of iron oxide, alumina, and other oxide impurities. Several types of commercial kieselguhrs were used as supports:

CATALYST MATERIALS AND SUPPORTS

Material	Al Pellets	Kies. Pellets	Al_2O_3 Powder	Carbon Powder	Kies. Powder	Multicel Powder	Flitercel Powder	Pure Metal	Special Support
Ru	1-15;18;20;21;24-31;37;38;43;44;57;95-98;105;107	51;52	22;23;45;62 110;111-114	64	60			46;48;50;53;54;56 116-119	108 (200-mesh SS gauze) 109 (200-mesh Ni gauze)
Rh	P-1		71	101;102				67	
Ir	16;17;72		68					74	
Os	81;99							49	
Pt			111;112	93			94		
Pd	78		100;115	103;104					
Ni (NiO)	39;40;88;105	19;32-36;65			47;61	89-91		55;58;75-77;83 120-122	
Ni on Spec.Supp.	66 (T-326)								
Ni Amine	69;70 (T-325)								
Co		41;42;79			63			86	
Ta_2O_5								82	
W								84	
Cb								73;87	
Nb_2O_5								80	
Mo								85	
MoO_3								92	
Pure Kies.		59							

Numbers indicate experimental test number

Figure 8 CATALYST MATERIALS AND SUPPORTS

a. Micro-cell E — Synthetic calcium silicate formed by reacting diatomite with lime. Surface area 175 m^2/gm, particle size $< 0.1 \mu$. Product of Johns-Manville Corp.

b. Filter-cel — Natural (uncalcined) diatomite. Surface area 10-15 m^2/gm, particle size 4-6 μ. Product of Johns-Manville Corp.

c. 000 Multi-cel — Diatomaceous earth. Surface area 46.1 m^2/gm, average particle size 10-12.5 μ. Product of Tamms Industries Co., Chicago, Ill.

The surface areas of several kieselguhrs range between 10 and 175 m^2/gm, while activated gamma alumina is 220 m^2/gm, and carbon is 800 to 2000 m^2/gm.

Pure metal powders and metal oxide powders used in the program were used essentially in the form obtained from commercial sources. The powders ranged from 80 to 250 mesh. The platinum family metals were obtained from manufacturers who deal in both catalysts and the pure precious metals. The other metals and metal oxides were obtained from commercial sources in the chemical and metallurgical industries.

The physical properties, support material and supply source for all the catalysts used are listed in the appendix.

4.3.2 Catalyst Tests

The basic operating conditions for measuring catalyst performance were as follows:

CO_2 Flow (one-man) : 2.5 lbs/day = 430 cc/min at 1 atm., 70°F

H_2 Flow : 4.0 to 4.5 x CO_2 Flow

Reactor Pressure : 14.7, 10.0 and 5.0 psia

The full-size stainless steel reactor, No. 1-S, was built and sized to operate under these conditions, while the three glass reactors, Nos. 1-, 2-, and 3-G, were built for special purposes and were not designed specifically to operate under all of the above conditions.

During operation of the system the objective of performance testing primarily was to relate the degree of carbon dioxide conversion with temperature, at varied flow rates and pressures for different catalysts and supports. The degree of carbon dioxide conversion is the fraction of carbon dioxide entering which reacts with hydrogen to form methane and water. From the reaction equation,

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O$$

the degree of conversion may be calculated from a measurement of the inlet and outlet CO_2 concentrations. Assuming the product water is condensed out,

the degree of conversion is:

$$X = ((a - b))/((a - 4ab))$$

where X = fraction of inlet CO_2 converted

a = mole fraction of CO_2 in inlet gas

b = mole fraction of CO_2 in outlet gas with product water condensed out.

In the actual system where the inlet CO_2 concentration, a, was fixed, the degree of CO_2 conversion was read directly from the outlet gas CO_2 concentration, b.

The graph in Figure 9 shows the degree of CO_2 conversion versus CO_2 outlet concentration for several inlet CO_2 concentrations.

The 1-S reactor was designed to allow operation at one-man capacity with measurements of carbon dioxide conversion, reaction temperature and pressure, and system heating and cooling requirements. As will be described subsequently, accurate catalyst bed temperature measurements were not possible, and smaller reactors such as the 2-G and 3-G were needed to decrease the catalyst bed size and permit accurate temperature measurements.

Based on the results of the literature search, ruthenium and rhodium were indicated initially as the best catalysts for low temperature CO_2 methanation. Consequently both to test reactor operation and to gain experience with the test monitoring system several preliminary tests were initiated with these catalysts using the 1-G glass reactor.

At a CO_2 flow of approximately 0.2-man capacity (~90 cc/min), with 1/8-inch pellets of 0.5% rhodium on alumina, conversion began at 400°F, and reached 6% at 500°F. With similar pellets of ruthenium, CO_2 conversion began at approximately 300°F and completed between 380° and 450°F. These tests showed no unusual results and testing was consequently changed to the full-size 1-S reactor.

4.3.2.1 Reactor No. 1-S - A series of twenty-one tests were run in the 1-S reactor. Ruthenium, iridium, and rhodium on 1/8-inch alumina pellets, and nickel on 1/8-inch kieselguhr pellets were tested in this series. These catalysts were supplied by commercial manufacturers.

The best performance with this reactor at one-man CO_2 capacity (approximately 471 cc CO_2/min, H_2:CO_2 of 4.6) was with ruthenium where 99% CO_2 conversion occurred at approximately 540°F, 1 atm., and a space velocity of 470 hr^{-1} (Test #8). Space velocity is Total Gas Volume Flow Rate, S.T.P/Total reactor Volume.

The other catalysts tested under the same conditions and providing the same conversion required reaction temperatures of 675°F for nickel-kieselguhr (#19) and over 750°F for rhodium (#18). Iridium promoted no conversion up to

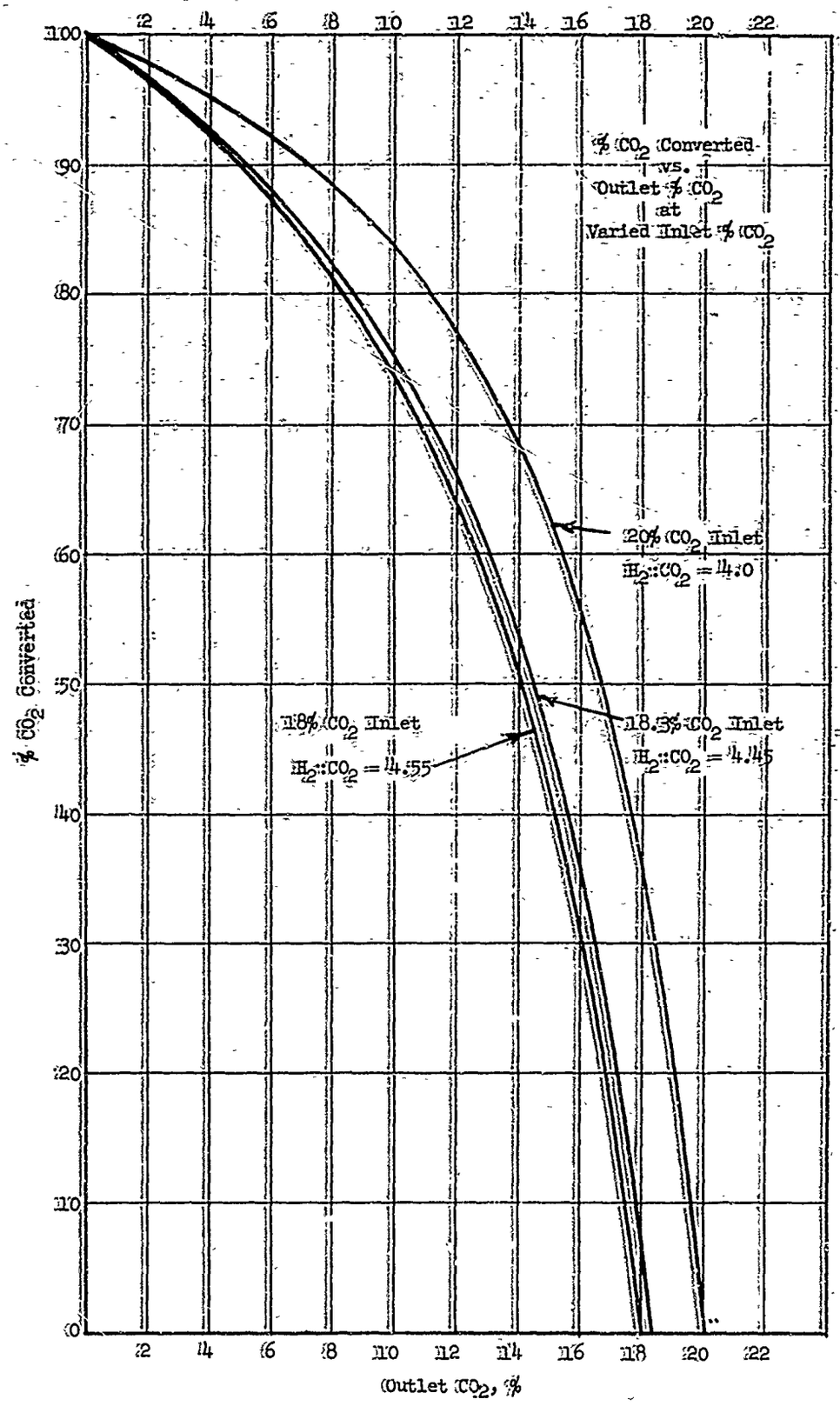

Figure 9 CO_2 CONVERSION VS. CO_2 OUTLET CONCENTRATION

700°F (#16, 17). The temperatures indicated are the maximum in the catalyst bed and parts of the bed were at considerably lower temperatures. However, any decrease below this maximum temperature resulted in lowering of the percentage of CO_2 converted.

The temperature in the bed of the 1-S reactor ran typically as follows:

	Inlet End	Middle	Outlet End	
Wall	395	540	299	(Test #8)
Center	445	503	275	

The middle of the reactor ran at higher temperatures than either end of the 8-inch long reactor. Once the reaction reached complete CO_2 conversion the maximum temperature remained in the middle. However, at the start of the reaction the highest temperature was at the center of the inlet end.

The temperature profile in the reactor remained relatively constant during sustained operation if alternate heating and cooling were properly regulated. When cooling was not provided the reaction temperature would rise spontaneously at one-man CO_2 feed rates, and in some tests rose readily to 750°F and would have gone higher if allowed.

The large temperature gradients in the 1-S reactor prevented accurate correlation of a true reaction temperature with CO_2 conversion, and also created difficulties in closely controlling the temperature by either heating or cooling the reactor.

The best performances with the 1-S reactor at varied fractions of one-man capacity for these catalysts were as follows, for 99% conversion at 1 atm., and H_2:CO_2 of 4.6:

	CO_2 cc/min	Space Vel. hr^{-1}	Reaction Temp., F°	Test No.
Ruthenium	472	470	540	8
	382	380	475	11
	221	220	500	15
	117	117	525	21
Nickel-Kies.	472	470	675	19
	382	380	640	19
	221	220	530	19
	117	117	410	19
Rhodium	472	470	> 750	18
	382	380	740	18
	221	220	667	18
	117	117	585	18

Again ruthenium provided the best overall preformance although the required reaction temperature did not decrease as anticipated with decreasing space velocities, as it did with nickel and with rhodium. This disparity

in temperatures is attributed to the fact that the temperature measurements for ruthenium were made in four different tests with varying changes in the considerable temperature profile in the 1-S reactor. The temperature measurements were sequential during the same tests for nickel and for rhodium, and showed at least a consistent trend within each test.

4.3.2.2 Reactor No. 2-G - The difficulties in measuring a true reaction temperature in the 1-S reactor led to the construction of the 2-G reactor. A series of twenty-three tests (Nos. 22 to 44) were run with the 2-G reactor. Ruthenium and nickel, each on 1/8-inch alumina, cobalt and nickel, each on 1/8-inch kieselguhr, and ruthenium on alumina powder were tested in this series.

The 2-G reactor volume was approximately 0.25 of the 1-S reactor volume. A flow of 117 cc CO_2/min (in terms of space velocity, 420 to 470) was equivalent to a one-man CO_2 flow in the 1-S reactor. At this space velocity the maximum temperature in the reactor for 99% CO_2 conversion at 1 atm. and H_2:CO_2 of 4.6 with ruthenium on 1/8-inch alumina was 480°F at the outlet of the catalyst bed (Test #24).

The verticle temperature gradient was 100°F in the reactor, but this was not unexpected because the inlet gases were not preheated. The front end of the bed heated the inlet gas and ran at approximately 480°F. Since the reaction is exothermic the true temperature for 99% conversion in the 2-G reactor bed was between 380° and 480°F for this test. The radial temperature gradient was approximately 10° - 15°F.

To decrease the vertical temperature gradient the space velocity in the reactor was lowered to approximate values of 420, 330, 130, and 65 hr^{-1} in the 1-S reactor. The best performances for approximately complete conversion (95-99%) at 1 atm. and H_2:CO_2 of 4.45 were:

	CO_2 Flow cc/min	Space Vel. hr^{-1}	Reaction Temp., °F	Test No.
Ruthenium	117	418	405-480	24
1/8" Alum.	38	132	430-470	31
	19	66	388-412	28
Nickel	95	330	465-532	36
1/8" Kies.	38	132	330-390	35
	19	66	360-400	34

In these tests the vertical temperature gradient in the bed decreased to 40°F at 66 hr^{-1} and 75°F at 418 hr^{-1}. The true reaction temperature was thus more closely related to CO_2 conversion.

In later tests of ruthenium on 1/8-inch alumina (#37,38) the degree of CO_2 conversion dropped off sharply to between 40% and 75% at temperatures and velocities which previously were adequate for 99% conversion, i.e., 480°F and 418 hr^{-1}. Reactivation of the ruthenium by reduction with hydrogen at 300°F for 170 hours raised the conversion to 85% of expected capacity (#43), but only temporarily, since in the next test the conversion dropped to 48% (#44), at 415-423°F and 66 hr^{-1}.

In all the tests with the 2-G reactor the temperature and conversion values were allowed to come to equilibrium and stabilize by operating the system for sufficiently long periods up to one hour at each temperature level.

Tests with ruthenium on alumina powder showed no conversion even up to 700°F. Nickel on 1/8-inch alumina only after reduction with hydrogen at 650°F for 16 hours provided 38% conversion at 643°F and 66 hr^{-1}. Cobalt on 1/8-kieselguhr provided 83% conversion at 677°F and 66 hr^{-1}.

Several additional factors were observed during this series of tests:

a. Decreasing the H_2:CO_2 ratio from 4.4 to 4.0 decreased conversion from 96% to 80% (#36)

b. Carbon dioxide desorbs from the catalyst surface when the bed temperature is lowered, giving a temporary, apparent but false change in CO_2 conversion (#26,33).

c. CO_2 conversion increases with temperature increase up to a particular temperature. Above this temperature conversion either increases no further or actually decreases (#35, 37, 38).

d. With both nickel and cobalt catalysts some carbon monoxide (0.15-0.40%) was formed in the 500°-550°F range.

The catalyst volume in the 2-G reactor (83 cc) was too large for testing samples of pure precious metal catalyst powders. The 3-G reactor (10 cc) was built primarily for this purpose.

4.3.2.3 Reactor No. 3-G - A series of 79 tests were run with the 3-G reactor. Of this number 54 tests were run on commercially supplied catalysts, and 25 on catalysts prepared in the MRD laboratories. Both vertical and radial temperature gradients in the catalyst bed approximated 10°F.

The majority of tests in the series were made on ruthenium and nickel in several forms on various supports, and as pure metal powders. The remaining members of the platinum group and cobalt were tested on various supports, and with the exception of platinum and palladium, as pure metals. In addition, tungsten, columbium and its oxide, molybdenum and its oxide, and tantalum oxide were tested.

All of the catalysts tested with the exception of two were in the form of powders or 1/8-inch and 1/16-inch pellets. The two exceptions were ruthenium on two different metal gauze supports.

The best CO_2 conversion performance in all of the tests in the 3-G reactor was with 10 cc of ruthenium metal powder (150-200-mesh) which promoted over 99% conversion at 357°F, 1 atm., H_2:CO_2 of 4.45, and a space velocity of 310 hr^{-1} (Test #53). This performance was achieved only after the ruthenium was activated with nitric acid washing and air roasting as described in Section 4.3.3.1. The raw, unactivated, commercial ruthenium powder promoted no conversion of CO_2 up to 475°F; after reduction with hydrogen at 325°F for 16 hours it promoted only 87% conversion at 573°F (#46, 48). For comparison

purposes, 10 cc of ruthenium on 1/8-inch alumina pellets (used in earlier tests in the 2-G reactor) were similarly activated with nitric acid and air roasting and tested, but promoted 99% conversion only after the reaction reached 600°F; conversion was 0% at 357°F and did not actually start until 415°F (#57).

Ruthenium on kieselguhr powder provided 95% conversion at 575°F, and on alumina powder only 90% at 650°F (#60, 62). Ruthenium on carbon promoted no conversion up to 585°F (#64).

The second best performance in the 3-G reactor was with osmium metal powder (150-mesh) which promoted over 99% CO_2 conversion at 450°F under all the same conditions as with ruthenium metal powder, but at a space velocity of 620 hr^{-1} (Test #49). The osmium was activated only by reduction with hydrogen at 325°F for 16 hours. For comparison, osmium on 1/8-inch alumina pellets were tested after similar hydrogen activation but promoted only 78% conversion at 660°F; conversion did not actually start until the reactor temperature reached 500°F (#81). Further activation was attempted by nitric acid washing and air roasting but this completely removed the osmium metal from the alumina supports. Activation in this manner is dangerous because poisonous osmium tetroxide vapors can be generated.

The third best performance was with nickel which promoted 99% conversion at 500° to 520°F. Both nickel metal powder and nickel on kieselguhr powder and 1/8-inch pellets promoted the reaction (#65, 83, 91). However, the nickel metal powder required preparation by thermal decomposition of reagent grade nickel formate with subsequent hydrogen reduction, and storage in a CO_2 atmosphere until used in the reactor to prevent the highly pyrophoric nickel from spontaneously oxidizing and losing its catalytic properties. Unless these procedures and precautions were observed, i.e., use of reagent grade materials, hydrogen reduction, and carbon dioxide storage, this conversion temperature could not be attained with pure nickel metal.

A special commercial stabilized nickel amine originally provided 97% conversion at 465°F, but the test was of short duration, and after the catalyst was reduced in hydrogen at 325°F for 16 hours 97.5% conversion required 595°F (#69, 70).

Neither rhodium or iridium metal powders, pre-reduced with hydrogen, promoted any conversion up to 580°F (#53, 74). The other pure metals tested, columbium, tungsten, and molybdenum, showed meager or no conversion up to 650°F (#73, 84, 85).

An interesting phenomenon was noted with columbium. The metal powder as commercially supplied ranged from 80 to 200-mesh in size, and in this form did not promote CO_2 conversion. The metal was sieved and a sample with size 150 to 200-mesh was separated. This sample promoted 30% conversion at 660°F (#87), where no conversion occurred with the coarser sample (73).

Nickel on kieselguhr, either commercially available or laboratory prepared, required activation by hydrogen reduction, but did not require storage in a CO_2 atmosphere. Both pellets and powder performed equally well

in the 3-G reactor. The laboratory prepared nickel on kieselguhr involved nickel formate and ammonia as described in Section 4.3.3.3.

None of the other catalysts performed as well as ruthenium, osmium or nickel. A commercial cobalt catalyst on 1/8 x 3/16-inch kieselguhr provided 97% conversion but only at 657°F after activation with hydrogen at 325°F for 16 hours (#79). Pure cobalt metal powder promoted only 65% conversion at 650°F (#86).

The oxides of columbium, tantalum and molybdenum promoted no conversion up to 600°F (#80, 82, 92).

Among the members of the platinum group (excepting ruthenium) on various supports the best performance was with 5% rhodium on alumina powder which promoted 90% conversion at 650°F (#71). None of the other supported catalysts in this group showed any appreciable conversion capability.

Among the mixtures of powders made by grinding up the 1/8-inch alumina pellets having 0.5% platinum group coatings, the best performance was with a 50-50 mixture of ruthenium and palladium. This mixture promoted 98% conversion at 650°F (#114). Each of these powders alone promoted 83% (Ru) and 71% (Pd) conversion between 675° and 700°F (#110, 115). This indicated that a synergistic effect does take place with mixtures of the platinum metals.

The two samples of ruthenium deposited on the surface of 200-mesh stainless steel gauze, and 200-mesh nickel gauze provided no conversion up to 500°F, (#108, 109).

A long duration run was made with pure ruthenium metal powder to determine the relative life of this catalyst (#123). The run was continued for thirty (30) days. The ruthenium metal powder was a mixture of catalysts from runs #116 to #119. The required reaction temperature was 435°F for complete CO_2 conversion, although in previous testing, the required temperature was only 357°F (#53). The space velocity and H_2:CO_2 ratio were 310 hr^{-1} and 4.45:1, respectively.

During the entire thirty-day run, the catalyst provided continuous and complete CO_2 conversion with no signs of deterioration or change in the catalyst. After the test was stopped the physical appearance of the catalyst was essentially unchanged, although the ruthenium did appear somewhat lighter in color than at the start of the test. This slight color change may have been due to desorption of surface water from the catalyst, brought about by the sustained high temperature.

During the last three days of the test, hydrogen sulphide gas was introduced into the carbon dioxide and hydrogen feed line to determine the effects, if any, of poisoning the catalyst. All of the Group VIII metals catalysts, both the platinum group and Fe, Co and Ni, have been reported susceptable to poisoning by sulfur compounds, such as H_2S, mercaptans and carbon disulfide, particularly when these metals were used in the Fischer-Tropsch synthesis of paraffins from carbon monoxide and hydrogen.

The hydrogen sulfide was injected into the inlet gas stream which was

flowing at a total rate of 50 cc/min of CO_2 and H_2. At 15-minute intervals a quantity of 0.01 cc of H_2S was injected into the stream for a period of six hours on three successive days. This amount of H_2S produced no change in the CO_2 conversion effectiveness of the ruthenium catalyst.

4.3.3 Preparations of Catalysts

The results of the literature search and of initial experimental tests indicated that ruthenium was the catalyst with the greatest potential for successfully promoting complete and low-temperature reduction of carbon dioxide. On this basis ruthenium was selected for experimental laboratory preparation to determine the effects of different preparations and supports on CO_2 reduction. Platinum and nickel were also selected for laboratory preparation. A total of twenty-five tests were made with laboratory-prepared catalysts, all in the 3-G reactor. The numbers of these tests are: 51, 52, 55, 56, 58, 59, 60, 61, 75, 76, 77, 80, 83, 89, 90, 91, 94, 95, 96, 97, 98, 106, 107, 108 and 109.

Several different methods were used for preparing catalysts. These were:

a. Decomposition of a thermally unstable compound or H_2 reduction to give a finely divided compound such as a pure metal or metal oxide from a metal salt.

b. Impregnation of a carrier or support material with a solution of the catalyst salt, followed by reduction or ignition of a mixture, leaving pure metals or metal oxides deposited on materials with high surface area to volume ratios.

c. Precipitation of a catalyst material from solution, with subsequent washing of extraneous ions, and final conversion by heating or drying.

d. Co-precipitation of a catalyst material and support material from solution to provide a greatly dispersed catalyst with a high activity.

e. Application of films of active metal catalysts to surfaces by actual evaporation of the metal with condensation upon the support surface.

In addition to these chemical preparations, various platinum group catalysts from commercial sources on 1/8-inch alumina pellets were ground to powder, approximately 100-150-mesh, and mechanically mixed in varying ratios of one metal to another, for measuring the effect of using mixtures of these metals as catalysts.

4.3.3.1 Ruthenium Preparations - To prepare solutions of ruthenium from the metal a special technique is required, since ruthenium metal is highly stable and unreactive with most acids and bases.

a. Preparation of K_2RuO_4, and Purified Ru Metal

Potassium ruthenate, K_2RuO_4 is prepared from ruthenium metal by mixing one part (by weight) of finely divided ruthenium, one part KNO_3, and ten parts KOH in a pure silver crucible and heating to fusion at approximately 900°F. The probable reaction is:

$$Ru + 2KNO_3 + 2KOH \longrightarrow K_2RuO_4 + 2NO + K_2O + H_2O$$

A silver crucible and silver stirring spatula are required since silver is not attacked by the fused alkali.

No particular precautions are necessary during this preparation other than observing the temperature minimum. At 820°F, the reaction does not proceed even after several hours. At 900°F, the conversion is practically complete after 10 minutes, but to insure complete conversion the mixture should be maintained at this temperature for a minimum of one hour. When the reaction is nearly complete, the melt surface becomes jet-black, and lustrous in appearance.

On completion of the reaction the crucible and contents are cooled to room temperature, followed by dissolution of the solidified mass in distilled water. The resulting solution is deep red in color.

The solution is heated to boiling and an excess of ethyl alcohol added drop-wise. A finely-divided black precipitate of $Ru(OH)_4$ immediately forms. The reaction involved is:

$$K_2RuO_4 + 4C_2H_5OH \longrightarrow Ru(OH)_4 + 2C_2H_5OK + 2CH_3CHO + H_2.$$

The precipitate is then separated from the solution by means of a Buchner funnel.

The precipitate is washed between ten and fifteen times with distilled water until a neutral pH is indicated. A dilute HNO_3 solution may be used initially to neutralize any remaining KOH, but this is unnecessary if the precipitate is thoroughly washed.

On completion of the washing step, the precipitate is placed in an evaporating dish and baked at 200°F in air. This converts the hydroxide to RuO_2.

To obtain a purified finely-divided ruthenium metal, the resultant RuO_2 is reduced in a stream of hydrogen at 300°-400°F for four to five hours. The resultant metal particle size is between 150- and 250-mesh (.0030-.0015-inch) (Test #56).*

To obtain a finely-divided ruthenium metal-kieselguhr catalyst, a quantity of kieselguhr approximately 100 times the total weight of ruthenium is added to a K_2RuO_4-water solution followed by addition of ethyl alcohol. This brings

* Numbers in parentheses indicate the number of the experimental test in which the catalyst was tested as listed in the appendix.

about the precipitation of $Ru(OH)_4$ in the presence of the kieselguhr support. The product is washed repeatedly until no traces of KOH remain, and then is dried at 200°F to convert the precipitate to RuO_2, which can then be converted to ruthenium metal on kieselguhr by reduction in H_2 at 300°F.

The powder can be used either in this state or pressed into pellets, although pellets made from this powder are difficult to form, have little mechanical strength, and disintegrate in water ((#51, 52, 60).

b. Vapor Deposition with RuO_4

Ruthenium tetroxide, RuO_4, was prepared according to the following procedures.

A small quantity of RuO_2 ((prepared as described previously)) is placed in a distillation flask, followed by the addition of an excess of concentrated perchloric acid. The mixture is heated to gentle boiling at which time the flask becomes filled with yellow gaseous RuO_4. The probable reaction is:

$$2RuO_2 + HClO_4 \longrightarrow 2RuO_4(g) + HCl$$

The RuO_4 was driven off and condensed as a yellow solid in a flask at the temperature of dry ice-acetone. The RuO_4 was then dissolved in cold water.

On completion of the reaction, the solution of RuO_4 was heated to room temperature and transferred to an alumina support by means of the system shown schematically in Figure 10.

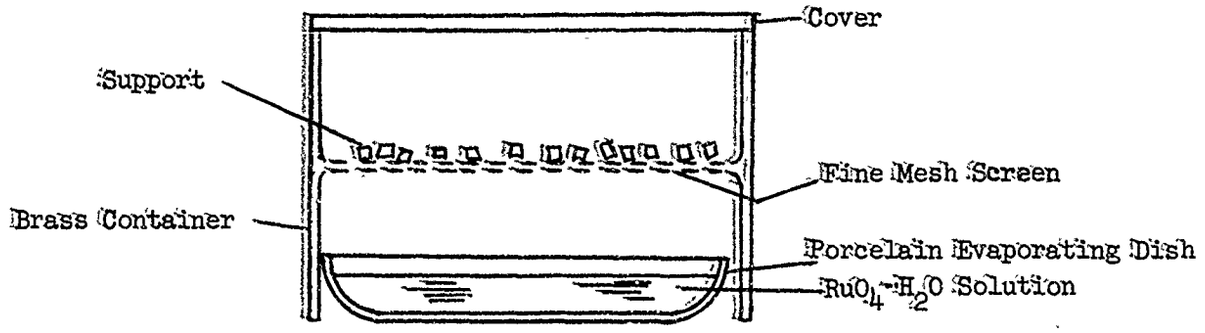

Figure 10 RuO_4 Deposition System

Heating the RuO_4 solution released an RuO_4 vapor and the vapor collected on the surface of the support, at the same time converting to a shiny black deposit after a few hours. This deposit is believed to be RuO_2. The deposit clings tenaciously to the pellet, being removed only by scratching the surface

with a sharp instrument ((#95, 96, 106, 107)).

An alternate method was tried for the preparation of RuO_4 based on general information in the literature indicating the RuO_4 could be prepared directly from the metal by heating in oxygen. This method was attempted with no success over a temperature range from 70° to 500°C.

c. RuO_4 Impregnation

The alumina supports ((both 1/8-inch spheres and cylinders)) were immersed directly in liquid RuO_4, removed from the liquid, and allowed to dry in air. The yellow RuO_4 again changed color to a dull, light grey deposit on the surface of the support, differing markedly from the vapor-deposited supports ((#97)).

d. RuO_2 - Perchloric Acid Impregnation

On completion of an RuO_4 preparation, as described above, a viscous, black liquid remains in the distillation flask. When all remaining water is driven off by heat, the remaining liquid containing dissolved or highly subdivided ruthenium is jet-black in color and similar to concentrated perchloric acid in viscosity.

When Al_2O_3 pellets are immersed in this liquid and then removed and heated to 600°F in hydrogen, a poorly adherent black deposit remains ((#98)).

e. Electrolytic Deposition of Ruthenium

Attempts were made to deposit ruthenium black on nichrome ribbon using a platinum anode, and the following electrolytes:

((a)) 0.5 gm $RuCl_3$ + 0.5N HCl,

((b)) 0.5 gm $RuOH_4$ + 1 gm sulfamic acid in 100 ml H_2O

((c)) 5×10^{-3}M $Ru(NO)Cl_3$ + 0.5N HCl.

Cases ((a)) and ((c)) produced dull grey, poorly adherent deposits over a range of current values from 25-200 milliamperes, at room temperature. In case ((b)) no plating occurred for conditions identical to those in ((a)) and ((c)). Rather, ruthenium metal collected in the bottom of the cell directly below the cathode.

f. Activation of Ruthenium Metal Powder

The following treatment was found to markedly improve the catalytic activity of ruthenium metal powder.

Ten grams of ruthenium ((approximately 7 cc)) was placed in a beaker containing 75 ml of 5N HNO_3. The mixture was heated to 105°C, held at temperature for five minutes and then cooled to room temperature. The mixture was then washed repeatedly with distilled water until pH measurement indicated

neutrality. The metal was then dried.

Next, the ruthenium was placed in a silver crucible and heated in air to 400°C. The ruthenium was maintained at this temperature for one hour, at which time it was cooled rapidly to room temperature, and subsequently used for testing.

g. Deposition of RuO_2 on Stainless Steel and Nickel Gauze

Ruthenium dioxide was deposited on 200-mesh stainless steel gauze by wrapping the stainless steel tightly around a strip of nickel foil, and then immersing it in a solution of RuO_4 and H_2O. A black deposit formed after a few minutes which became powdery and poorly adherent on drying. No deposition took place when the stainless steel was placed alone in the RuO_2-H_2O solution, indicating that the nickel probably acted as a reducing agent. This material, on testing, was found to be catalytically inactive however. After testing, inspection showed that the original powdery deposit had been replaced by a grey-brown, tenacious deposit ((#108)).

Ruthenium dioxide was deposited from an RuO_4-H_2O solution on 200-mesh nickel gauze, in the same way as on stainless gauze, but gave much the same results as the stainless-steel-RuO_2 material. One exception noted was that the RuO_2 deposit, subsequent to testing appears to have been replaced by metallic ruthenium instead of the dull, grey-brown deposit observed with the stainless-steel ((#109)).

4.3.3.2 Platinum Preparation

Preparation of Platinum Black on Filter-Cel:

This preparation is based on the reaction

$$PtCl_4 + HCOO^- Na \longrightarrow Pt + 4CO_2 + 4NaCl + 2H_2$$

In practice, a 0.85 gm sample of $PtCl_4$ was dissolved in 250 ml distilled water followed by the addition of 4.5 gm Filter-cel which results in the formation of a slurry. A 0.85 gm amount of NaCOOH is subsequently added. This effects the reduction of the $PtCl_4$ to the black which is adsorbed on the Filter-Cel. The Filter-cel is then washed and filtered repeatedly in a fritted glass, Buchner funnel. After washing, the platinum-black-Filter-cel mixture is dried at 150°F in air. The dried powder is finally ground to 200-mesh particle size and tested ((Test #94)).

4.3.3.3 Nickel Preparations

Various methods were used to prepare both pure nickel metal and nickel on support media. Nickel is readily soluble in bases and acids, and its salts are easily converted to the metal or its oxide.

Pure nickel powder was prepared in several ways, from the carbonate, oxide, and formate. Only after careful preparation from reagent grade materials, and without exposing the precipitated nickel to air was any degree

of conversion achieved. Nickel in its pure state is readily oxidized by air and rapidly loses its catalyzing properties. The preparations are as follows:

a. Reagent grade nickel oxide was heated in hydrogen at 700°F in a Vycor glass tube for 16 hours to provide pure nickel metal powder, approximately 200-mesh, for use in testing ((#77)).

b. Nickel Carbonate on Kieselguhr.

In this method, a 0.1 molal solution of $NiSO_4$ is prepared, followed by the addition of a catalyst carrier such as kieselguhr or activated charcoal. Next, hot Na_2CO_3 solution is added to the $NiSO_4$-carrier mixture, precipitating $NiCO_3$, which is adsorbed on the carrier. The $NiCO_3$-carrier is separated from the solution and washed repeatedly with distilled water until all detectable $SO_4^{=}$ has been removed.

After washing, the $NiCO_3$-carrier is evaporated to dryness. The product becomes granular and hard and it is necessary to grind and sieve the compound for use as a catalyst.

The dried product is now placed in an alumina crucible and heated to 700°F in air, which brings about the decarbonization of the apple-green $NiCO_3$, forming green-black NiO. The conversion seems to be complete after approximately 1-1/2 hours. The NiO can now be reduced to Ni in hydrogen at 200°F for 16 hours completing the preparation.

The carrier materials used in this preparation included Multicel, ((#61)) and activated carbon. Multicel worked satisfactorily, adsorbing $NiCO_3$ with ease; the activated carbon, however, adsorbed insignificant amounts, obviating its use as a carrier.

c. Nickel Formate Decomposition to Nickel and Nickel on Kieselguhr

$Ni(OH)_2$ was precipitated from $NiCl_2$ solution with NaOH and washed with distilled water. The $Ni(OH)_2$ slurry was then dissolved in a slight excess of HCOOH and the solution evaporated to dryness obtaining crystallization of nickel formate.

The nickel formate was then heated to 500°F in a hydrogen atmosphere which resulted in its slow decomposition to nickel metal according to the reaction:

$$Ni(HCO_2)_2 \xrightarrow{\Delta} Ni + H_2 + 2CO_2.$$

The decarbonization was allowed 2-1/2 days to go to completion. The resulting nickel powder weighed slightly less than the theoretical yield indicating the possibility that some moisture was originally present in the formate crystals ((#55, 58, 75, 76)).

In preparing nickel on kieselguhr the above described procedure was used with the modification that Multicel was added to the $Ni(OH)_2$ after it was dissolved in a slight excess of HCOOH. The weight of Multicel used was approximately equal to the weight of the nickel in the $Ni(OH)_2$ (Test #89).

In another nickel formate decomposition, the hydrogen feed was interrupted when, during the heat-up, the formate reached 500°F. Gas evolved from the decomposing formate at several hundred cc/min. The temperature of the reaction remained at 500°F for approximately one hour and then rose to 900°F, apparently because the decomposition reaction had ended and no gas flow was available to dissipate the heat from the reactor heater. The nickel powder so obtained was allowed to reduce two hours at 600°-700°F in hydrogen, followed by cooling to room temperature in a CO_2 atmosphere. The nickel was then stored in CO_2 until used (#83).

In another preparation of nickel on kieselguhr the following procedure was used.

A three gm quantity of reagent-grade $Ni(COOH)_2$ was added to 200 ml of concentrated NH_4OH solution, bringing about the dissolution of the $Ni(COOH)_2$. Since $Ni(COOH)_2$ is insoluble in H_2O, but very soluble in concentrated NH_4OH, it seemed advisable to use this medium for dissolution, since it would be of little difficulty to drive off the NH_4OH as NH_3 and H_2O at a later stage of the preparation, thereby leaving the nickel uncontaminated, in its final state.

Next, 20 cc (3 gm) of Multicel was added to the $NH_4OH - Ni(COOH)_2$ solution, forming a thin paste. This paste was placed in an oven and heated to 200°F to remove NH_3 and H_2O and finally decomposed at 500°F, in air, to reduce the $Ni(COOH)_2$ to metallic nickel. The reaction equation for the reduction is given:

$$Ni(COOH)_2 \longrightarrow Ni + CO_2 + H_2O + CO$$

This procedure effects the preparation of approximately 50% (by weight) nickel - 50% Multicel catalyst of reasonable purity and surface area (#90,91).

d. Nickel Powder from Nickel Nitrate

Nickel nitrate was thermally decomposed to form nickel trioxide, which in turn was reduced at 800°F-1000°F in a hydrogen ambient. The resultant nickel metal, however, formed a compacted mass unsuitable for use as a catalyst.

4.3.4 Discussion of Test Results

4.3.4.1 Catalyst Performance - The best catalyst performances are summarized in the table below for the 2-G and 3-G reactors. Ranking is based on essentially complete carbon dioxide conversion (97%-99%) at the lowest reaction temperature, and at equivalent space velocities and $H_2:CO_2$ ratios. Conversions below this range and at temperatures above 575°F were not included.

Rank	Catalyst	Reactor	% Conversion	Temp. °F.	Space Vel. hr^{-1}	$H_2:CO_2$ Ratio	Test No.
1	Ruthenium metal powder	3-G	99	357 (435)	310 (310)	4.45	53 (116, 117)
2	Osmium metal powder	3-G	99	450	620	4.45	49
3	Ruthenium on 1/8" Al_2O_3	2-G	99	480	418	4.6	24
4	Nickel metal powder	3-G	99	500	310	4.45	83
5	Nickel on Multicel pwdr.	3-G	99	520	310	4.45	91
6	Nickel on 1/8" Kieselguhr	3-G (2-G)	99 (96)	520 (532)	310 (330)	4.45	65 (36)
7	Nickel on Kies. powder	3-G	97 (98)	485 (537)	310	4.45	121 (47)

In several other tests 97%-98% conversion was achieved at temperatures ranging between 390°-458°F but at lower space velocities. Nickel on 1/8-inch kieselguhr provided 98% conversion at 390°F and at 132 hr^{-1}, but as shown above this same catalyst required 520°F at 310 hr^{-1}. Similarly ruthenium on 1/8-inch Al_2O_3 provided 98% conversion at 412°F but at 67 hr^{-1}.

These performances are based on essentially complete conversions at the lowest temperature in the best test for each category of catalyst in its most active state. For example, ruthenium on 1/8-inch Al_2O_3 pellets provided 99% conversion at 480°F in test #24. In subsequent tests the identical catalyst sample gave lower conversions with other conditions equal indicating a slow decrease in the catalytic capacity of this sample.

In tests which provided less than 99% conversion no higher conversion could be achieved than the figures shown, even when the temperature was increased. Also, in several instances the conversion decreased on increase of temperature.

All of the catalysts in this summary table, with the exception of two, were either pure metal powders or commercial catalysts from industrial catalyst manufacturers. The nickel metal powder in test #83 was prepared in the MRD laboratories, as was the nickel on kieselguhr powder in test #91. Both laboratory prepared catalysts required special preparative procedures as discussed in Section 4.3.3.3.

4.3.4.2 Effects of Laboratory Preparations - During the course of

the experimental program ruthenium and nickel appeared to give the highest conversion performances. Consequently laboratory preparations of potential catalysts were concerned mainly with these two metals on several different supports.

Ruthenium was prepared on kieselguhr powder, 1/8-inch alumina pellets, stainless steel gauze, nickel gauze, and as pure metal.

Pure metal powder was prepared from a solution of a ruthenium salt, primarily to determine if there were any differences in performance between the laboratory prepared sample and the commercially supplied metal. Both were powders of very closely similar size, 150- to 200-mesh. The prepared metal powder provided 71% conversion at 470°F, approximately 100°F higher than achieved with commercially supplied metal, but at a space velocity approximately five times as high (#56). Ruthenium on kieselguhr powder provided 95% conversion at 575°F (#60), which is approximately 100°F higher than was needed for commercially supplied ruthenium on alumina pellets. None of the other ruthenium preparations provided any appreciable conversion. In general, the laboratory preparation of ruthenium did not provide as high performance as the commercial metal powder or supported catalysts.

Nickel was prepared on kieselguhr powder and as the pure metal. After several different preparation techniques were used, pure nickel metal powder was prepared from a salt of the metal. The prepared nickel metal powder provided 99% conversion at 500°F, and the nickel on kieselguhr 99% conversion at 520°F (#83, 91). Use of reagent-grade materials, reduction with hydrogen, and storage in a carbon dioxide atmosphere were essential to provide this performance. These performances are considered slightly better than with commercial nickel catalysts primarily because the degree of conversion was slightly higher (99% vs 97% in tests #83, 91 vs. #47, 121) at similar space velocities and temperature ranges.

In summary, the effects of the laboratory preparations on CO_2 conversion performance were as follows:

1. The laboratory preparations of ruthenium, both as metal powder and as supports, required approximately 100°F higher operating temperatures for complete CO_2 conversion than did commercially supplied ruthenium.

2. The laboratory preparation of nickel both as metal powder and on supports did not require as high operating temperatures for complete CO_2 conversion as did commercially supplied catalysts.

3. For both ruthenium and nickel, the laboratory-prepared powders provided lower reaction temperature than supported metals.

4. For both metals on supports the best support material was kieselguhr.

4.3.4.3 Experimental Temperature, Composition, Pressure, and Space Velocity Effects - The effect of temperature upon the reaction was generally as expected from the information collected during the literature search, and from the theoretical considerations of the chemical

equilibrium relationship.

Various references showed that the minimum temperature at which complete CO_2 reduction was possible was 310°F with a ruthenium catalyst, and that the reaction was initiated at approximately 200°F. In test #53 with ruthenium the reaction began at 273°F and completed at 357°F, bearing out the effect of activation temperature on initiating and completing the CO_2 reduction in the expected 300° to 400°F temperature range.

The chemical equilibrium relationship indicated that essentially complete CO_2 conversion was possible up to a given temperature, and that conversion would decrease if all of the reactor bed were above this temperature. This was shown true in several tests where increasing the reaction temperature did not increase conversion and actually caused a decrease in some instances, with attendant formation of CO as an undesirable end product. This behavior was demonstrated in tests #35, 37, 38, 54 and 89.

For an H_2:CO_2 ratio of approximately 4.4:1 the equilibrium relation indicates the maximum temperature for 99% complete CO_2 conversion is 610°F. In accordance with this, test #35 showed a drop from 96% conversion at 500°F to 85% at 685°F.

Theoretically, from equilibrium considerations, it is impossible to achieve essentially complete (> 99%) conversion at temperatures above 300°F for a H_2:CO_2 ratio of 4:1. This was verified in test #36 where 96% conversion required 532°F at a H_2:CO_2 ratio of 4.45:1. When the ratio was decreased to 4.0:1, the conversion dropped to 80% at 537°F. Thus a 10% excess of hydrogen in the feed allowed approximately complete CO_2 conversion with all other conditions remaining equal. In addition, the excess of hydrogen has been reported desirable to prevent the formation of CO which acts effectively as a transient inhibitor of the CO_2 reduction process.

The effect of decreased pressure on the reaction was shown theoretically to be relatively slight for essentially complete CO_2 conversion. Tests with ruthenium metal powder indicated only a slight change from 99% to 98% conversion when the reaction pressure was changed from 14.7 psia to 5.0 psia, holding the temperature constant (#117, 118, 119). This change is in very close agreement with the behavior predicted from chemical equilibrium theory.

The effect of space velocity with all other factors remaining equal was to decrease the fraction of CO_2 conversion as the space velocity increased (#8, 11, 18, 19, 24).

4.4 Optimum Catalyst

4.4.1 Catalyst Selection

On the basis of the results of the experimental testing program ruthenium has developed as the optimum catalyst. The factors which determined the optimum catalyst were: (1) completness of CO_2 conversion, (2) minimum reaction activation temperature, (3) catalyst configuration and support material, (4) reaction pressure, (5) space velocity, and (6) chemical inertness and non-toxicity.

The primary comparison of the three most efficient catalyst materials, ruthenium, osmium, and nickel was discussed in Section 4.3.4.1. On the combined basis of CO_2 conversion, reaction temperature and space velocity, ruthenium and osmium metal powders could be rated as approximately equal, both being well above pure or supported nickel.

The pure metal powders in all cases performed better than when supported. However a comparison of ruthenium and osmium on supports indicated supported ruthenium as far superior to supported osmium.

In addition, osmium metal is relatively easily oxidized to the tetroxide which is an extremely poisonous gas. Although ruthenium tetroxide is also a highly poisonous gas it is very difficult to form from the pure metal.

In tests of ruthenium and nickel at reduced pressures, ruthenium and nickel both performed approximately equally on the basis of pressure variation, but again, ruthenium operated at a lower reaction temperature level than nickel. (Ru at 435°F; 99% conversion at 14.7 psia, 98% at 5 psia. Ni at 485°F; 97% at 14.7 psia, 93% at 3 psia).

4.4.2 Catalyst Properties and Design Data

The pure ruthenium metal powder has a bulk density of 85 lb/ft^3, and the particles have an average diameter between 0.002 and 0.003 inches. The pressure drop through the particles with upward flow through an unrestrained bed is approximately 3 inches W.G. per inch of bed length at a linear velocity of 0.33 ft/min. For restrained beds (such as would be required for zero-gravity operation, or for downward flow) larger particle sizes are essential.

In a one-man system at a space velocity of 310 hr^{-1}, approximately two pounds of the ruthenium powder tested would be required for the reactor bed. Based on the thirty-day duration test performed, the weights of catalyst needed for 100-, 200-, and 300-day missions would be 6.6, 13.3 and 20 lbs, respectively. These are maximum weights and could be reduced depending on the success of more extensive duration tests. During the duration tests, the catalyst appeared unaffected by the short periodic injection of hydrogen sulphide into the feed gases.

For a one-man reactor (designed approximately similar to the 1-S reactor) weighing seven pounds and containing two pounds of catalyst, the heating requirement to initiate the reaction would approximate 350 Btu, which is the estimated heat input to raise the reactor and catalyst to 350°F. The cooling rate requirement to maintain the system at this temperature level is 167 Btu/hr, which is the approximate value of the heat of reaction for one-man capacity. Cooling would be accomplished both by heat losses through insulation and by circulation of a cooling fluid around the reactor; the amount of fluid coolant needed is thus dependent upon the final reactor and insulation design.

SECTION 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

On the basis of the combined phases of the complete program to determine ar applicable low temperature-high yield catalyst for promoting the Sabatier reaction, the following conclusions have been reached.

a. The optimum catalyst was determined to be pure ruthenium metal powder, unsupported, average particle diameter 0.002 to 0.003 inch, bulk density 85 lb/ft^3.

b. With this catalyst the minimum operating temperature for complete (>99%) single-pass CO_2 conversion was 357°F, at 14.7 psia when the space velocity was 310 hr^{-1}, and the H_2:CO_2 ratio was 4.4 as a minimum.

c. Pretreatment of the ruthenium metal powder with 5 normal nitric acid washings at 200°F and air oxidation at 750°F was necessary to activate the catalyst.

d. Supported ruthenium, both commercially supplied and laboratory prepared, did not provide as high CO_2 conversion as did pure ruthenium metal with all other factors being equal.

e. Ruthenium metal could not be oxidized to any of its oxides, particularly to poisonous ruthenium tetroxide (RuO_4), when roasted in pure oxygen up to 800°F, demonstrating a highly desirable inertness to oxidation.

f. Continuous operation for a thirty-day period with ruthenium metal powder caused no changes in CO_2 conversion or in the catalyst material. On this basis, for a one-man reactor, a maximum of two pounds of catalyst are adequate for a thirty-day mission.

g. Pure ruthenium, nickel and osmium metal powders in all instances provided higher CO_2 conversion than any of their supported forms, either as pellets or as powders.

h. Ruthenium on alumina (Al_2O_3) showed a gradual loss of catalyzing capacity with passage of time, and could not be effectively re-activated by nitric acid washing and air roasting.

i. Osmium metal powder was rated as the second best performing catalyst with complete conversion at 450°F and a space velocity of 620 hr^{-1}, with all other parameters the same as for ruthenium metal in b.

j. Nickel metal powder was rated as the third best performing catalyst with complete conversion at 500°F with all other parameters the same as for ruthenium metal in b.

k. All of the platinum group metals promoted varying degrees of CO_2 conversion either as pure metals or on various supports, with the exception of iridium. Neither pure powder nor alumina supported iridium provided any CO_2 conversion.

l. Pure metal tungsten powder, and the oxides of columbium, tantalum, and molybdenum, in powder form, did not promote CO_2 conversion at temperatures up to 650°F.

m. Pure metal powders of cobalt, columbium, and molybdenum provided only partial (15-65%) CO_2 conversion at 650°F.

n. Combinations of powders of 1) ruthenium on Al_2O_3 and palladium on Al_2O_3, and 2) ruthenium on Al_2O_3 and platinum on Al_2O_3, provided higher CO_2 conversion than any of the single materials alone.

o. Operation at 5 psia versus 14.7 psia caused a decrease in CO_2 conversion from 99% to 98% with the ruthenium catalyst.

p. A stoichiometric H_2:CO_2 ratio is not adequate for rapid single-pass complete CO_2 conversion. A ratio of approximately 4.4 appears adequate.

q. Operation at temperatures in excess of 600°F caused a decrease in CO_2 conversion at an H_2:CO_2 ratio of 4.4 in accordance with predictions based on equilibrium theory.

r. Treatment of catalysts with hydrogen at 300°F to 600°F for extended time periods (16 hr or longer) in general is not adequate alone to activate or regenerate ruthenium or nickel catalysts. Additional specific preparations and pretreatments are necessary.

s. The 1-S reactor with ruthenium on Al_2O_3 pellets sustained one-man CO_2 conversion with no electrical input, and required controlled cooling to prevent excessive temperature rise.

t. Operation of the 8" long x 2" diameter one-man reactor (No. 1-S) demonstrated that large temperature gradients existed in the reactor bed, with the axial gradients ranging from 100° to 250°F, and the radial gradient from 25° to 150°F.

u. Continuous infra-red detection of the inlet and outlet CO_2 concentration was required for accurate correlation of CO_2 conversion with reaction temperature.

5.2 Recommendations

Based on the observations and conclusions drawn from the complete program the following recommendations are made concerning the use, operation, evaluation and future testing of catalyst materials and a full-size reactor for the Sabatier reaction.

a. The full-size one-man reactor should be designed to minimize the

temperature gradient within the catalyst bed and operate as nearly isothermally as possible, by using devices such as heat transfer fins, or special reactor shapes to aid in rapid removal of the heat of reaction.

b. A longer duration test should be made with the optimum catalyst, and the effects of poisoning should be further explored.

c. When the optimum catalyst, ruthenium metal powder, is to be used in a zero-gravity environment, it should be used in the form of particles larger than 0.002 to 0.003-inch in diameter, to eliminate the high pressure drop which would result from packing of the smaller sized particles.

d. Pure ruthenium metal powder should be tested in larger grain sizes to determine the relation between CO_2 conversion and pressure drop for varied particle diameters.

e. Additional controlled tests with ruthenium metal powder should be run at varied space velocities since this information is of importance in trade-off studies for the design of a full-size reactor.

f. Mixtures of pure ruthenium metal powder, with other metals such as platinum, palladium, and rhodium should be tested as potential improved catalysts to determine if the mixtures of metals demonstrate the synergistic effects noted with powdered mixtures of these metals on alumina supports.

g. Similarly metal powders of alloys of ruthenium and other members of the platinum group should be tested as potential improved catalysts.

h. Although osmium has the potentiality of creating a poisonous by-product if it is inadventently oxidized, its catalyzing capabilities should be further investigated.

i. The reactor bed should run isothermally and not be cooled by the inlet gases. Heat of reaction should be removed externally, not by the reaction gases. The inlet gas to outlet gas heat exchanger in a full-size reactor should be separate from the reactor catalyst bed.

APPENDIX A

LITTERATURE REFERENCES

Catalyst	Product	Conditions	Author	Chem. Abstract	Reference
$Cu-Al_2O_3$	MeOH		Impatieff & Monroe	40:1140^6	JACS, 67, 2168-71 (1945)
Not Specified	MeOH		Smith and Hirst	24:5586^2	IEC 22, 1037 (1930)
60Cu-35.6ZnO-4.4Cr_2O_3	MeOH	100 Atm; 200°C	Parpekhov & Shokol	32:3244^6	Mem. Inst. Chem. Ukrain. Acad. Sci 4, 205-12 (in Germ 212-13)(1937)
16ZnO-Cr_2O_3-82Cu	MeOH	100 Atm; 200°C	Parpekhov & Shokol		Mem. Inst. Chem. Ukrain. Acad. Sci 4, 205-12 (in Germ 212-13)(1937)
8ZnO-$Al(OH)_3$-0.1V_2O_5-3KOH	Higher Alcohols	220 Atm; 350°-425°	Bocharova, Kan-Kogan	32:4518^5	Petrova Khim. Tvordogo Topliva, 8, 1107 (1937)
8ZnO-$Al(OH)_3$-0.1V_2O_5-0.1MoO_3-3KOH	Higher Alcohols	220 Atm; 350°-425°	Bocharova, Kan-Kogan	32:4518^5	Petrova Khim. Tvordogo Topliva, 8, 1107(1937)
Mn, Fe, Cu, Cr, Cd and Mixtures	Higher Alcohols		Ryoken Fujii	41:3750d	J. Chem. Soc. Japan 64, 1103 (1943)
Lithium Borohydride in ether solution	$HCHO_2$	70% yield	Brown & Burr, Jr.	NSA 2-1341	AECD-2482nd Decl Feb. 18, 1949
Lithium Aluminum Hydride	$HCHO_2$		Finholt and Jacobson	AD49470b	JACS, 8 May 1952
Raney Nickel	$HCHO_2$	80°, atm. press.	Farlow & Adkins	30:83^3	JACS, 57, 2222 (1935)
TiO_2, ZrO_2, CeO_2	Petroleum	5 ml/hr yield; atm. press. 180°C	Shinjirokodama	24:4376^5	J. Soc. Chem. Ind Japan 33, 202, (1930)
Not Specified	CO	340°, 376°, 410°	Giona, Passino, Toselli	53:19535 L	Ingegnere 33, No. 2, 129(1959)
W(hot filament)	CO		Srikantan	25:1149^1	J. Indian Chem. Soc. 7, 745-57 (1930)
Zn-Cu-Al	CO	325°C; 1700 lbs; 4% CO	Boomer & Morris	26:1180^3	JACS 54, 407 (1932)
Electrical Discharge	CO		Peters & Kuester	24:4708^9	Z. Physik. Chem. 148, 284-303 (1930)
Not Specified	CO		Bahr, Alhandl	24:5207^2	Kenntnis Kohle 8, 217-9; Chem. Zentr., 1929, II, 3263
Hot Filaments	CO		Srikantan	25:867^2	Rev. Trav. Chim. 49, 1146(1930)
Ni-Thoria	CH_4	350°C, 15 psi	Morikawa, Kimoto & Abe		Bul. Chem. Soc. Japan, 16, 229 (1941)
Not Specified	CH_4 and hydrocarbons	240°-350°, 10-30 atm.	Kolbel & Ackermann	49:P4972i	U.S. 2,692,274
Moly Oxide-Thorium Oxide	CH_4	8-15% yield, 30 atm. 400°C	Bahr, Abhandl		Kenntnis Kohle, 12, 292 (1937)
Al_2O_3-Moly Oxide	CH_4 and Paraffins	High Pressure and Temp.	Bahr, Abhandl		Kenntnis Kohle, 12, 292 (1937)

Catalyst	Product	Conditions	Author	Chem. Abstract	Reference
Ru	CH_4	Start at 100°C, Atm. Press. 100% CH_4	Fischer, Bahr, Meusel	30:3401[5]	Ber. 69B, 183-6 (1936)
Ru and alkalis	CH_4 and hydrocarbons	170°C, Atm. Press.	Fischer, Bahr, Meusel	30:3401[6]	Ber. 69B, 183-6 (1936)
Ru powder	CH_4	100°C, Atm. Press >95%	Fischer, Bahr, Meusel	30:3967	Brenn-Chem. 16, 466 (1935)
Ru-Th asbestos	CH_4	100°C, Atm. Press >95%	Fischer, Bahr, Meusel	30:3967	Brenn-Chem. 16, 466 (1935)
Ru + $CaCO_3$ or Rb_2CO_3	Hydrocarbons and small amounts of CH_4	170°C, Atm. Press	Fischer, Bahr, Meusel	30:3967	Brenn-Chem. 16, 466 (1935)
Ni (Reduced)	CH_4	500°-750°F Atm. Press.	Binder	45:7858e	U. of Mich. Microfilms, Pub. No. 2381
Ni (Reduced)	CH_4	500°-750°F Atm. Press.	Binder and White	45:3331b	CEP, 46, (1950) p. 563
Barker's medium (fermentation)	CH_4	50% yield, Fermentation	Bokova, Garibyants	53:22719c	Mikrobiologiya 28 272-3 (1959)
Not Specified	CH_4		Chandler, Burghardt, Walden, Taylor	TPA-N62-11326	Isomet Rpt. 5007 PPR 4-61, 4th rpt. 15 Sep-15 Mar, (1960-1961)
Ru	CH_4	100% yield	Burke, Meinschein		Rev. Sci. Instr. 26, 1137 (1955)
Cu, Ni, Cu-Ni Alloys	CH_4	200-500°C; Atm. Press.	Cratty,	52:7832a	Univ. Microfilms Publ. #23429, 119pp Dissertation Abst. 18, 411 (1958)
Cu, Ni, Cu-Ni Alloys	CH_4	200-500°C; Atm. Press.	Cratty, Russel	52:10863a	JACS, 80, 767, (1958)
Ni	CH_4	540°F-750°F; 2-30 Atm.	Dew	48:12664a	U. of Mich. Microfilms, Publ #8294 14, 1054, (1954)
Ni-Kieselguhr	CH_4		Dew, White,	49:3508h	IEC 47, 140(1955)
"Rhodium Black"	CH_4	100% yield; Other condition are not indicated	Duparc, Wenger, Urfer	20:5[a]	Helvetica Chim. Acta. 8, 609 (1925)
Oil Microflora	CH_4		V. Rudokimov	53:22847e	Mikrobiologiya 28, 594-7 (1959)
Ru	CH_4	98% yield; 475°C Btch; 100-40 psi	A. Fairhall, W. Scholl, Y. Takashima	55:20534b	Rev. Sci. Instr. 32, 323-5 (1961)
Ni	CH_4	0.1-1 atm; 180°-300°C	Nicolai, Hont, Jungers	41:4699b	Bull. Soc. Chem. Belges 55, 160-76 (46)
Fe	CH_4	300°C; small yield	Kuster,	30:7790[6]	Brennstoff-Chem. 17, 203-6 (1936)
Fe	CH_4	800°-900°F	Edwin Layng	43:p4446g	U.S. 2, 465, 462 Mar. 29, 1949
Ni and various promoters	CH_4		Medsforth	17:3271[2]	J.C.S. 123, 1452 (1923)
Cu-activated Co	CH_4 and hydrocarbons	175°-300°, 1 atm Press.	W. Russell and G. Miller	44:8616b	J.A.C.S. 72 (1950) 2446-54
Ni	CH_4	electrolytic	C.A. Palladino, R. E. Shearer, and J.C. King	PA-N62-11559	TPA-N62-11559-MSAR-62-36, 2nd Qtr. Status Rpt. Jan 1-Mar 31, 1962.

Catalyst	Product	Conditions	Author	Chem. Abstract	Reference
Ni-Kieselgahr-Mgo	CH_4	Atm. Press; 180°-250°C; 84-5%	W. Rottig	56:P1694h	Ger 1:110;147
Ni-Thoria	CH_4		Russell and Taylor	220:325[55]	J. Phys. Chem. 29, 1325-41 (1925)
Ni-Cr(III) Oxide	CH_4	160°-180°	M. Sölc	58:11998c	Collection Czech. Chem. Commun. 27, 2621-7 (1962) (in german)
Ni	CH_4	125°-325°	Vlasenko	56:6700	Kinetika and Kataliz 2, 528-8 (1961)
Fe-+10--100% Cu	Hydrocarbons			53:22845a	Ger 1, 1002,746 (2/21/57)
Not Specified	CO	Red heat		1:2747	
Fe, Co, Ni	CH_4		Mayer, Hensëling	44:2724[3]	J. Gasbel, 52, 1166-94, 1238-82
Carbon (heated)	CO		Holland, T.	8:235[4]	Gas World, 59, 671-2
Not Specified	CO		Pier	55:2352[6]	Z. Elektrochem 16, 897-903
Not Specified	CO		Neumann, K.	9:1384[1]	Z. Ver. Deut. Ing 1482-4, 1501-4 (1914)
Fine Grained Filter Paper	CH_4		Zenghëlis, C.	14:2286[1]	Compt. Rend, 170 883 (1920)
Porous Membrane	HCHO		Zenghëlis, C.	14:2740	Compt. Rend, 171 167-70 (1920)
Cobalt Oxide	Benzine		Ganswindt, Neueste Erfin	15:3204[1]	
Powdered Ni	CH_4	800°	Müller, Barch,	17:3295	Z. Anorg. Allgem. Chem. 129, 321-2 ((1923)
Ni on MgO granules	CH_4	180°; atm. Press 5 cc/min gas flow, 95-3% yield at 328°	Neumann and Jacob	119:1083[1]	Z. Elektrochem 30, 557-76 (1924)
Not Specified	MeOH		Anilin and Fabrik	P19:2673[32]	German Patent
W	CO	953°-1303°	Hinshelwood, and Prichard,	119:3198	J. Chem. Soc. 127 1546-52 (1925)
Not Specified	CO	1000°	Prichard, and Hinshelwood	119:3411[1]	J. Chem. Soc. 127 806-11 (1925)
Luminous discharge	HCHO	Small yield	Boehm, Bonhoeffer	20:3645[6]	Z. Physik. Chem., 119, 385-99 (1926
Pt gel	HCHO, MeOH	15 psi	Morris, Reyerson	22:345[5]	Proc. Indiana Acad. Sci., 36, 203-6 (1927)
Permutoid amino siloxenes			Kautsky	22:1890[1]	Naturwissen schaften, 16, 204, (1928)
Fe		Atmospheric Pressure	Decarriere, and Antheaume	27:4632[28]	Compt. Rend. 196 1889 (1933)
Cobalt	CH_4		Chakravarty, and Ghosh	20:860	Quart. J. Ind. Chem. Soc. 4, 431 (1925)
Ni	CH_4		Sabatier and Senderens		J. Chem. Soc. 88, 333, 401 (1905)
Co	CH_4		Sabatier and Senderens		J. Chem. Soc. 88, 333, 401 (1905)

Catalyst	Product	Conditions	Author	Chem. Abstract	Reference
Ni	CH_4		Schuster, Panning and Buelow	30:3967[9]	Brennstoff-Chem. 16, 358 (1935)
Ni	CH_4		Sabatier, and Senderens		Comp. Rend. 134, 514 (1902)
Ni-Co	CH_4	150°-400°; Good yield with CO_2	Koch, and Kuster	27:5154[3]	Brennstoff-Chem. 14, 245 (1933)
$CoSO_4$-CuO-MnO	CH_4		Morgan	30:8147[3]	Bul. Soc. Chim. Belg. 45, 287 (1936)
Ni-Porcelain	CH_4		Jochum	8:1659	J. Gasbeleuchtt, 57, 73, 103, 124, 149 (1914)
Ni-porcelain	CH_4	500°C; atm. press	Pease and Chesebro	22:2139[4]	J.A.C.S. 50, 1464 (1928)
Ni-porcelain-ceria	CH_4	322-395°C	Randall and Gerard	23:814	Ind. Eng. Chem. 20, 1335 (1928)
Ni-porcelain	CH_4	322-395°C	Randall and Gerard	23:814	Ind. Eng. Chem. 20, 1335 (1928)
Ni-pumice	CH_4	471°, 15 psi, flow system	Ghosh, Chakravarty Bakshi	26:648	Z. Electrochem 37, 775 (1931)
Ni-Thoric-Ceria-Carbon.	CH_4		Chakravarty	32:2818[b]	Sci. and Culture 3, 396 (1938)
	C (Graphite)		Randall, Shiffler	24:333[5]	Ind. Eng. Chem. 21, 941, (1929)
Ceria-promoted, Cu-contg., Co with $CO_3^{=2}$, Cl^-, $SO_4^{=2}$, $S^{=2}$, Salts	Liquid and Gaseous Hydrocarbons	Atmospheric Pressure	Milford, and Russell		J.A.C.S. 74, (1952)
GP VIII metals (atomic No. >>26) in comb. with difficulty red. oxides, e.g., ThO_2 or MgO	Hydrocarbons and oxygenated organic compds.		McGrath	48:P3381f	U.S. 2,637,739, May 5, 1953
Co-Fe alloys	Hydrocarbons; CO	Flow, 6 ℓ/hr; 200°-400°	Stowe and Russell	48:6100b	J.A.C.S. 76, 319 (1954)
Fe	Hydrocarbons	Flow; 6 ℓ/hr; 200°-400°	Stowe and Russell	48:6100b	J.A.C.S. 76, 319 (1954)
Fe, Co, Ni on MgO Al_2O_3, MnO, TiO_2	Hydrocarbons and oxygenated organic compds.		Riblett and McGrath	53:P1688b	U.S. 2,850,515, Sept. 2, 1958

PATENTS

Catalyst	Reference	Author	Title
Platinum Metal-Ceramic Carrier	U.S. 3,125,539 Eng.	Teague, E. D.	"Ceramic Catalyst Having a Sprayed Coating of a Platinum Family Metal"
Ruthenium-Platinum Metal Mixtures	U.S. 3,055,840	Koch, Jn., J.H.	"Ruthenium - Containing Catalysts and Methods of Making said Catalysts and Increasing Their Activity"
Noble Metals	U.S. 3,134,732 Engel 15 Sept 64	Kearby, K. K., Thorn, J. P., Hinlicky, J. A.	"Reactivation of Nobel Metal Catalysts With Gaseous Halogens"
Noble Metal	U.S. 3,235,699	Henzog, N. Kabisch, G.	"Regenerating a Hydrogenation Catalyst"
Ruthenium	Inorg.Chem.,1964 3, (7), 1057-1058 Pt. Metals Rev. Vol. 8 #4 Oct. 1964	Trent, D. E., Paris, B. Krause, H. H.	"Vapor Deposition of Pure Ruthenium Metal from Ruthenocene"
Platinum Group	U.S. 3,125,539	Norton Co.	"Ceramic Catalyst Flame Sprayed with a Platinum Group Metal"
Platinum Group Metals	French Patent 1,346,159	Brown, H. C., Brown, C. A.	"Finely Divided Platinum Metal Catalyst"
Al_2O_3	U.S. 3,009,885 RTB Mar. 1962 Vol. 6 #4	Bertalacchi, R.S.	"Aluminum Catalyst of Increased Surface Area"
Noble Metals	U.S. 2,945,757	Hoehstrom, J.	"Recovery of Noble Metals from Catalyst Composites"
Ruthenium	Pt Metals Rev. Bishop Co. Vol. 3 No. 2		"Ruthenium Catalyst for Paraffin Wax Synthesis
Ruthenium and Osmium	Pt Metals Rev. Bishop Co. Vol. 6 No. 1		"Ruthenium and Osmium as Hydrogenated Catalysts"
Ruthenium	Pt Metals Rev. Bishop Co.Vol.1 #1		"Electrodeposition of Ruthenium"
Pt Group Metals	U.S. 2,885,369 (May 5, 1959)	Tetes, J. W., Keith, C. D.	"Catalyst Preparation"

GENERAL REFERENCE TEXTS

(1) Advances in Catalysis (Academic Press, Inc., New York, N.Y.) Volumes I - XIV

(2) Catalysis (Reinhold Publishing Corp., N.Y.; P.H. Emmett, Edition) Volumes I - VII

(3) Annotated Bibliography on Ruthenium, Rhodium, and Iridium as Catalysts (The International Nickel Co., Inc., N.Y.; Compiled by A. Rea and M. Bebbington) (1959).

(4) H. Storch, N. Golumbic, R. Anderson, The Fischer-Tropsch and Related Syntheses, John Wiley & Sons, Inc., N.Y.

(5) C. A. Jacobson, Encyclopedia of Chemical Reactions, Reinhold Publishing Corp., N.Y., Volumes III - V (1953).

APPENDIX B

EXPERIMENTAL TESTS

Test	Reactor	Catalyst	CO_2 Feed cc/min	$H_2:CO_2$	% CO_2 conv.	Catalyst Temp. °F	Space[a] Vel, Hr^{-1}	Stay Time[b] Sec.	Remarks
1 (4/21)	1-S	Ru on 1/8" Al (335 cc)	471	4.6[c]	49[c]	350. (mid-cent)	470	7.6	Temp. measured at middle center of bed only. 471 cc/min = 1-man CO_2 output. Reactor insulated and not cooled.
2 (4/22	1-S	Ru on 1/8" Al	471	4.6[c]	99[c]	320 (mid-cent)	470	7.6	Temp. controlled with heater only, manually. Temperature is minimum which still allows 99% CO_2 conversion. Reactor uninsulated and not cooled.
3 (4/28)	1-S	Ru on 1/8" Al	471	4.6[c]	99[c]	705 (top-cent)	470	7.6	Temp. measured at six points. Top, Mid, Bot. at wall and center. Highest temp. occurs at top-center, but this appears to be the controlling temperature. There is a 500°F vertical gradient. No cooling air; uninsulated.
					97[c]	665 (top-cent)			
4 (4/29)	1-S	Ru on 1/8" Al	471	4.6[c]	99[c]	500 (mid-cent)	470	7.6	The max. temp. is initially at mid-center, for 99% conv., but moves up to top-center and remains. Gradients as before. No cooling air; uninsulated.
					99[c]	525 (top-cent)			
5 (4/30)	1-S	Ru on 1/8" Al	471	4.6[c]	86[c]	535 (mid-cent)	470	7.6	Used cooling air for first time. Max. temp. point moved from mid-center to top center as before. Cooling creates sharp temp. changes, making control difficult.
					98[c]	505 (top-cent)			
6 (5/1)	1-S	Ru on 1/8" Al	471	4.6[c]	97[c]	550 (Mid-wall)	470	7.6	Added temperature controller to control heater. Used cooling air to cycle reaction and keep temp. as low as possible. Control is difficult. Cycling creates 15° to 200°F temp. fluctuations. Conversion approximate 41% at 445°F.
7 (5/4)	1-S	Ru on 1/8" Al	470	4.6[c]	93[c]	575 (top-cent)	470	7.6	Controller now turns off heater and turns on cooling air simultaneously at a given control temperature. Reactor was insulated with a 1/2" layer of asbestos around body only; ends still uninsulated. Control at a single level is still difficult.
8 (5/5)	1-S	Ru on 1/8" Al	470	4.6[c]	99[c]	540 (mid-wall)	470	7.6	Simultaneous control of heat and air creates 100-200° temperature cycling. Reactor temperature profile continually shifts, making relation of conversion to temp. difficult. Vertical gradient is 200° to 250°F, radial gradient is 150° to 25°F.
					99[c]	585 (top-cent)			
9 (5/13)	1-S	Ru on 1/8" Al	470	4.6[c]	99[c]	650 (top-cent)	470	7.6	With no cooling, reactor rose to 650° at top center; with manual cooling conversion dropped off to 94% at 535°F. (top-center).
10 (5/18)	1-S	Ru on 1/8" Al	220	4.6[c]	99[d]	417 (top-cent)	220	16.5	Flow reduced 50%. A 4-inch layer of fiberglass was added around reactor. With no cooling reaction was nearly self-sustaining at 417°F, but cooled to 391° where only dropped to 92%. A 0-0.2% carbon monoxide LIRA was added to monitoring system in outlet gas line.
11 (5/19)	1-S	Ru on 1/8" Al	380	4.6[c]	99[d]	475 (top-cent)	380	9.5	At 3/4-man flow reaction sustained itself down to 475°F but began to fall off at 440°F. Reactor was air-cooled after reaction achieved 99% conversion.
12 (5/20)	1-S	Ru on 1/8" Al	470	4.6[c]	99[d]	640 (top-cent)	470	7.6	Reaction is self-sustaining for 1-man flow down to 640°F, but fell off to 93% at 600°F when cooled by air.

a. Space Velocity = Total (CO_2 + H_2) Volume flow rate at 70°F, 1 atm./Catalyst bed volume.

b. Stay Time = 3600/space vel.

c. Gas composition measured by Beckman GC-2 Gas Chromatograph

d. Gas composition measured with LIRA infrared CO_2 analyzer, 0-4% CO_2

Test No.	Reactor No.	Catalyst	CO_2 Feed cc/min	$H_2:CO_2$	% CO_2 conv.	Catalyst Temp. °F	Space Vel. hr^{-1} [a]	Stay Time [b] Sec.	Remarks
13 (5/22)	1-S	Ru on 1/8" Al	470	4.6[c]	98[d]	723 (top-cent.)	470	7.6	Top 2-1/2" of reactor contains catalyst. Lower 5-1/2" now filled with aluminum metal 1/8" pellets. The top-center inlet temp. ran 75-100° higher than when reactor is filled with catalyst.
		plus inert metal pellets	220	4.6[c]	99[d]	590 (top-cent.)	220	16.5	
14 (5/27)	1-S	Ru on 1/8" Al	470	4.6[c]	99[d]	690	470	7.6	This test showed the temp. required for self-sustained reaction running at 690°, or 50°F higher than previously noted in run No. 12. Catalyst was left open for four days prior to use.
15 (5/28)	1-S	Ru on 1/8" Al	220	4.6[c]	99[d]	500	220	16.5	Catalyst was reduced overnight at 300°F. Reaction is not quite self-sustaining. Conversion falls off at 500°F.
16 (5/29)	1-S	Ir on 1/8" Al	220	4.6[c]	0[d]	700	220	16.5	No appreciable conversion of CO_2 was found with Iridium catalyst. Iridium was out-gassed under vacuum at 700°F.
17 (6/1)	1-S	Ir on 1/8" Al	117	4.6[c]	0[d]	700	117	30.8	No appreciable conversion of CO_2 even at 1/4-max capacity with Iridium. Iridium was reduced over-night at 300°F with hydrogen.
18 (6/2)	1-S	Rh on 1/8" Al	117	4.6[c]	99[d]	585	117	30.8	Rhodium reduced over-night at 300°F with H_2.
			220	4.6	99	667	220	16.5	
			380	4.6	99	740	380	9.5	
			470	4.6	99	>750	470	7.6	
19 (6/3)	1-S	Ni on 1/8" Kies.	117	4.6[c]	99[d]	410	117	30.8	Nickel-Kieselguhr reduced over-night at 300°F with H_2.
			220	4.6	99	530	220	16.5	
			380	4.6	99	640	380	9.5	
			470	4.6	99	675	470	7.6	
20 (6/4)	1-S	Ru on 1/8" Al	117	4.6[c]	96[d]	535	117	30.8	Test of Ruthenium capacity at 1/4-max CO_2 flow. Catalyst was not reduced.
21 (6/5)	1-S	Ru on 1/8" Al	117	4.6[c]	99[d]	525	117	30.8	Catalyst reduced over-night at 300°F in H_2. Slightly higher conversion resulted at approximately same temperature.
22 (6/15)	2-G	Ru on Alumina Powder (40 gm 52 cc)	117	4.6[c]	0[d]	to 700	755	4.7	First tests with 2-G reactor, to test powder catalysts and smaller amounts of pellets. No conversion. Catalyst was pre-reduced with H_2 at room temp. for 3 hours to remove absorbed O_2.
23 (6/16)	2-G	Ru on Alumina Powder (52 cc)	117	4.6[c]	0[d]	to 700	755	4.7	Catalyst was reduced for 16 hrs at 300°F with H_2. Lack of conversion was not anticipated.
24 (6/18)	2-G	Ru on 1/8" Al (94 cc)	117	4.6[c]	99[d]	480	418	8.6	96 grams of Ru on Alumina pellets was tested for comparison with 1-S reactor, since smaller temp. gradients would be expected. Vertical gradient 150-200°F, radial 10-30°F.
			220	4.6[c]	99[d]	665	785	4.6	
			380	4.6[c]	99[d]	723	1360	2.6	
25 (6/19)	2-G	Ru on 1/8" Al (94 cc)	9	4.6[c]	--	to 500	32	113	At these low CO_2 and total flow rates temperatures could not be readily related to gas composition.
26 (6/24)	2-G	Ru on 1/8" Al (94 cc)	9	4.5[e]	--	To 360	32	113	Absorption and desorption of CO_2 from catalyst surface caused fluctuations in gas composition when temperature level was changed preventing correlation of temperature and conversion.
27 (6/25)	2-G	Ru on 1/8" Al (94 cc)	10	4.4[e]	99[e] 85(?)	340 410	35	106	Outlet and initial inlet composition measured with 0-30% CO_2 LIRA infrared analyzer. Temperature and outlet composition equilibria are required to relate accurately CO_2 conversion with temperature.

e. Gas composition measured by LIRA infrared analyzer, 0-30% CO_2

Test No.	Reactor No.	Catalyst	CO_2 Feed cc/min	$H_2:CO_2$	% CO_2 conv.	Catalyst Temp. °F	Space[a] Vel. hr^{-1}	Stay Time[b] Sec.	Remarks
28 (6/26)	2-G	Ru on 1/8" Al (94 cc)	19	4.4[e]	96[e]	407	67	54	Higher flow rates permit more rapid measurement of outlet gas composition.
29 (6/29)	2-G	Ru on 1/8" Al (94 cc)	19	4.4[e]	31[e] 20 13 0	310 250 200 175	67	54	Verification of lower temperature-conversion relation.
30 (6/30)	2-G	Ru on 1/8" Al (94 cc)	19	4.4[e]	98[e]	412	67	54	Check on run No. 28
31 (7/1)	2-G	Ru on 1/8" Al (94 cc)	38 (20½)	4.45[e]	95[e]	470	132	27	At this CO_2 flow rate 97% conversion occurred at 470°F, relatively a constant temp. throughout catalyst bed. Conversion started at 205°F. Conversion profile was verified by monitoring the outlet gas flow rates CO_2 conversion level was allowed to stabilize for each temp. and flow measurement
32 (7/2)	2-G	Ni and Kies., 1/8" (94 cc)	19	4.45[e]	92[e]	465	66	54	Harshaw No. Ni-0104, 58% Ni on Kieselguhr. Catalyst was not reduced during constantly changing conversion.
33 (7/6)	2-G	Ni and Kies., 1/8" (94 cc)	19	4.45[e]	95[e]	400	66	54	Catalyst was reduced for 60 hrs with H_2 at 300°F. Higher conversion achieved at lower temp., but results not clear due to ~~absorption and desorption~~ of CO_2 by the catalyst itself with temp. change.
34 (7/7)	2-G	Ni and Kies., 1/8" (94 cc)	19 (101)	4.45[e]	95[e]	400	66	54	Repeat & clarification of Run No. 33. Reaction started at 170°F Maximum conversion was 95% at 400°F.
35 (7/9)	2-G	Ni and Kies., 1/8" (94 cc)	38	4.45[f]	71[e] 98 96 85	340 390 500 685	132	27	Increased the CO_2 flow rate. Inlet and outlet CO_2 concentration now continually monitored by separate LIRA CO_2 analyzers. Checked effect of increased reactor temp. Above 500°F conversion appears to decrease at this flow and space velocity.
36 (7/10)	2-G	Ni and Kies., 1/8" (94 cc)	95	4.45[f] 4.0	34[e] 67 91 96 80	365 430 475 532 537	330	109	Increased flow requires higher temp. for conversion in comparison with previous run. Change in $H_2:CO_2$ ratio to 4.0 decreased conversion to 80% at 537°F.
37 (7/13)	2-G	Ru on 1/8" Al (94 cc)	95	4.45[f]	63[e] 84 84	502 540 595	330	109	Comparable test to No. 36 using Ru on 1/8" Al shows a higher temp. required. Max. CO_2 conv. was 84% at 540°F. Raising temp. additional 55°F to 595°, did not increase conversion.
38 (7/14)	2-G	Ru on 1/8" Al (94 cc)	95	4.45[f]	79[e] 87 87 84 84	538 557 575 622 702	330	109	Repeat of No. 37, but raising temp. to 700°F. Still did not increase conversion, but conv. did not decrease significantly either.
39 (7/15)	2-G	Ni on 1/8" Al (94 cc)	19	4.45[f]	0[e]	To 600	66	54	Catalyst is Harshaw No. Ni-0707, 14% Nickel oxide on Alumina. Did not form any CO_2, but did promote formation of 0.15% CO at 550°F as measured on 0.0 to 0.2% CO LIRA infrared detector.
40 (7/16)	2-G	Ni on 1/8" Al (94 cc)	19	4.45[f]	0[e] 30 38	380 558 643	66	54	Reduced Ni-0707 for 16 hrs at 650°F with H_2. Some CO_2 conversion achieved as shown. CO began to form at 400-500°F, and reached 0.4% at 643°F.

f. Gas composition measured with 0-28% CO_2 LIRA.

Test No.	Reactor No.	Catalyst	CO_2 Feed cc/min	$H_2:CO_2$	% CO_2 conv.	Catalyst Temp. °F	Space Vel. hr^{-1} [a]	Stay Time Sec.	Remarks
41 (7/17)	2-0	Co on 1/8" Kies. (9¼ cc)	19	4.45[c]	0[b]	325	66	5¼	Harshaw catalyst No. Co-0102, 38% cobalt on Kieselguhr, supplied as activated, reduced and stabilized was used without pretreatment with H_2.
					8	378			
					63	423			
42 (7/20)	2-0	Co on 1/8" Kies. (9¼ cc)	19	4.45[c]	0[c]	320	66	5¼	The catalyst was reduced with H_2 for 60 hours at 250°F. 0.04% CO was noted at 510°F
					44	388			
					75	510			
					83	677			
43 (7/21)	2-0	Ru on 1/8" Al (9¼ cc)	19	4.45[c]	0[c]	291	66	5¼	Ruthenium pellets were reduced in H_2 at 300°F for 170 hours prior to use in reactor. Conversion was not as high at comparable temperatures as in earlier tests which ran at even higher space velocities.
					46	363			
					30	348			
					51	370			
					92	441			
					97	458			
44 (7/22)	2-0	Ru on 1/8" Al (9¼ cc)	19	4.45[c]	32[c]	365	66	5¼	Reduced catalyst overnite with H_2 at 300°F. Repeat of previous run. Conversion was even lower than in Run 43. Activity of catalyst appears to be decreasing.
					40	392			
					48	423			
					75	490			
					77	557			
45 (7/23)	3-0	Ru on Alumina Powder (3.4 gm 5 cc)	9.5	4.45[c]	0[c]	400	620	5.8	Ruthenium on alumina powder (same sample used in test No. 22 & 23) was reduced for 120 hours with H_2 at 300°F. Test performed in 3-0" reactor
46-1 (7/24)	3-0	Ru Metal (1.6 cc)	9.5	4.45[c]	0[c]	400	1940	1.8	Ruthenium metal powder (150-200 mesh) was tested as supplied from (46-1) D.F. Goldsmith Co., and (46-2) Englehard Ind. No activation was performed.
46-2		Ru Metal (2.0 cc)	9.5	4.45	0	400	1550	2.3	
			3.6	4.45	0	475	590	6.1	
47 (7/27)	3-0	Ni on Kies. Powder (10 cc)	9.5	4.45[c]	23[c]	307	310	11.6	Pellets of Harshaw Ni-0104 Nickel on Kieselguhr were ground to powder, approx. 150 mesh and reduced for 16 hours with H_2 at 300°F.
					58	359			
					54	350			
					75	369			
					94	402			
					95	426			
					98	537			
48 (7/28)	3-0	Ru Metal Powder (10 cc)	9.5	4.45	0	325	310	11.6	Fresh ruthenium powder from Englehard Ind. (150-200 mesh) was reduced for 16 hours with H_2 at 325°F.
					~0	508			
					61	520			
					69	538			
					83	555			
					87	573			
49 (7/29)	3-0	Os Metal Powder (5 cc, 10 gm)	9.5	4.45	9	268	620	5.8	Fresh osmium powder from Englehard Ind. (150-200 mesh) reduced for 16 hours with H_2 at 325°F. This catalyst was first to show total conversion, >99% in any tests to date. Conversion temp. for the high space velocity and low stay time shown.
					34	348			
					83	394			
					94	420			
					>99	450			
					98	438			
					95	409			
50 (7/30)	3-0	Rh Metal Powder (2.1 gc, 10 gm)	9.5	4.45	0	300	1480	2.4	Fresh rhodium powder from Englehard Ind. (150-200 mesh) reduced for 16 hours with H_2 at 325°F.
51 (7/31)	3-0	Ru on 1/8" Kies. (10 cc)	9.5	4.45	0	325	310	5.8	Ruthenium was prepared on kieselguhr powder (0.5 gm of Ru on 13 gm of kieselguhr) and formed into 1/8" dia. x 1/8" long pellets. The pellets were reduced for 16 hours with H_2 at 300°F.
					35	472			
					47	500			
					86	385			

a. Gas composition measured with 0.40% CO_2 LIRA

Test No.	Reactor No.	Catalyst	CO_2 Feed cc/min	$H_2:CO_2$	% CO_2 conv.	Catalyst Temp. °F	Space Vel. Hr^{-1}	Stay Time Sec.	Remarks
52 (8/3)	3-G	Ru on Kies. Powder (10 cc)	9.5	4.45	0 30	488 562	620	5.6	Approx. 50% Ruthernium metal was mixed with Kieselguhr, both 200 mesh, to form a homogeneous mixture. Kieselguhr is 000 Hulticell, from the Tamms Co., Chicago, Ill. Catalyst was pre-reduced with H_2 at 300°F for 2 hrs.
53 (8/4)	3-G	Ru Metal Powder (10 cc)	9.5	4.45	0 17 71 88.5 94 99 100	273 296 328 334 343 343 357	310	5.8	The ruthenium is the same sample in Run No. 48. It was treated with boiling 5N · HNO_3 for 10 min., and then roasted in air at 650°F for 2 hrs.
54 (8/5)	3-G	Ru Metal (10 cc)	10.0	4.0	0 23 95 95	300 325 425 515	310	5.8	Same catalyst as Run 52. $CO_2:H_2$ ratio was lowered to 4.0; reaction temp. for 95% conversion increased to 425°F. Higher than 95% was not achieved up to 515°F.
55 (8/6)	3-G	Ni Metal (10 cc)	9.5	4.45	c 0	525 595	310	5.8	Nickel powder was prepared from nickel formate and reduced for 16 hours with H_2 at 350°F. During run some CO, up to 0.02%, was noted above 500°F.
56 (8/6)	3-G	Ru Metal (2 cc)	9.5	4.45	61 71	440 475	1550	1.2	Ruthenium was prepared by reduction of RuO_2 with H_2 at 300°F for 16 hrs. No treatment with HNO_3 or roasting in air.
57 (8/7)	3-G	Ru on 1/8" Al_2O_3 (10 cc)	9.5	4.45	0 17 78 89 94 99	415 455 510 550 570 600	310	5.8	Ruthenium on alumina was treated with boiling 5N · HNO_3 for 10 min. and roasted in air at 660°F for 2 hrs. Reduction with H_2 at 325°F for 16 hours followed.
58 (8/10)	3-G	Ni Metal (10 cc)	9.5	4.45	0	575	310	5.8	Same catalyst from run No. 55, but reduced for 60 hrs at 600-650°F with H_2.
59 (8/10)	3-G	Pure 1/8" Kies. Pellets (10 cc)	9.5	4.45	0	600	310	5.8	Pure 1/8" diam x 1/8" long Kieselguhr pellets were run as a blank to test catalytic properties of support material.
60 (8/11)	3-G	Ru on Kies. Powder (10 cc)	9.5	4.45	0 46 64 92 95	360 425 440 520 575	310	5.8	Ruthenium was deposited on kieselguhr powder, 45% Ru, 55% Kies., and reduced for 16 hrs at 350°F with H_2, prior to testing.
61 (8/12)	3-G	Ni on Kies. Powder (10 cc)	9.5	4.45	0 45 78	390 450 590	310	5.8	Nickel from nickel carbonate was deposited on Kieselguhr powder, 65% Ni, 35% Kies., and reduced for 16 hrs. at 375°F with H_2, prior to testing.
62 (8/13)	3-G	Ru on Al_2O_3 Powder (10 cc)	9.5	4.45	0 43 60 90	375 495 540 650	320	5.8	5% Ruthenium on Al_2O_3 powder (150-200 mesh) from Englehard Ind., was treated with boiling 5N · HNO_3 for 10 minutes and roasted at 650°F for 2 hrs in air, and then in H_2 at 325°F for 16 hours.
63 (8/14)	3-G	Co on Kies. Powder (10 cc)	9.5	4.45	0 50 65	300 460 610	310	5.8	Cobalt on Kieselguhr, Type Co-0108 Harshaw Chem. Co., in powder form was prepared by crushing commercially supplied pellets. Powder was reduced for 16 hrs at 300°F in H_2 prior to testing.
64 (8/17)	3-G	Ru on Carbon Powder (8 cc)	9.5	4.45	0	585°F	390	4.6	5% Ruthenium on carbon powder (150-200 mesh) from Englehard Ind. was treated with boiling 5N · HNO_3 and roasted in air for 2 hrs at 650°F, and then reduced for 60 hrs at 275°F with H_2.
65 (8/17)	3-G	Ni on 1/8" Kies. (10 cc)	9.5	4.45	0 23 55 78 86 95 99.5	300 350 375 390 400 475 520	310	5.8	58% Nickel on 1/8" Kieselguhr pellets, Harshaw No. Ni-0104 were reduced with H_2 at 550°F for two hrs. prior to testing.

Test No.	Reactor No.	Catalyst	CO_2 Feed cc/min	H_2:CO_2	% CO_2 conv.	Catalyst Temp. °F	Space Vel. Hr^{-1}	Stay Time Sec.	Remarks
66 (8/18)	3-G	Ni(T-326) 1/8"x3/16" Diam. (10 cc)	9.5	4.45	0 47 95 97.5	300 415 565 585	310	5.8	Girdler Co. T-326 reduced and stabilized Nickel on special support. No pretreatment.
67 (8/18)	3-G	Rh Metal Powder (10 cc)	9.5	4.45	0	580	310	5.8	Rhodium metal powder (150-200 mesh) as supplied from Englehard, was reduced with H_2 at 325°F for 16 hrs prior to testing.
68 (8/19)	3-G	Ir on 1/8" Al_2O_3 (10 cc)	9.5	4.45	0	570	310	5.8	Iridium metal powder (150-200 mesh) as supplied from Englehard, was reduced with H_2 at 325°F for 16 hrs prior to testing. Up to 0.2% CO was noted at 570°F.
69 (8/19)	3-G	Ni(T-325) 1/8"x3/16" Diam. (10 cc)	9.5	4.45	97	465	310	5.8	Girdler Catalyst Dept. of Chemetron Corp., Type T-325 reduced and stabilized nickel amine. No pretreatment. Temperature shown was under equilibrium conditions, with temperature and composition unchanged for over 1/2 hr.
70 (8/20)	3-G	Ni(T-325) (10 cc)	9.5	4.45	35 82 96 97.5 88	355 470 510 595 475	310	5.8	Same catalyst used in Run No. 69 but reduced for 16 hrs at 325°F with H_2
71 (8/21)	3-G	Rh on Al_2O_3 Powder (10 cc)	9.5	4.45	0 90	450 650	310	5.8	5% Rhodium on Alumina powder (150-200 mesh), Englehard, was reduced for 4 hrs with H_2 at 375°F.
72 (8/21)	3-G	Ir on 1/8" Al (10 cc)	9.5	4.45	0	600	310	5.8	0.5% Iridium on 1/8" Alumina pellets was treated for 10 minutes with boiling 5N $\cdot HNO_3$ and roasted in air at 600°F for 2 hrs, and then reduced with H_2 at 350°F for 16 hours.
73 (8/24)	3-G	Cb Metal Powder (10 cc)	9.5	4.45	0	635	310	5.8	Columbium metal (80-200 mesh) as supplied by Fansteel Corp., was reduced for 60 hrs. with H_2 at 325°F. Some CO was noted, 0.2%, during testing at 635°F.
74 (8/24)	3-G	Ir Metal Powder (10 cc)	9.5	4.45	0	550	310	5.8	Iridium metal powder (150-200 mesh) was reduced at 325°F with H_2 for 3 hours.
75 (8/25)	3-G	Ni Metal Powder (10 cc)	9.5	4.45	0 0 47 62 87	350 500 555 625 680	310	5.8	Nickel metal powder (approx. 200 mesh) was prepared from technical grade nickel formate, and after preparation kept in a CO_2 atmosphere to prevent nickel oxide formation. Catalyst was not H_2 reduced immediately before use.
76 (8/26)	3-G	Ni Metal Powder (10 cc)	9.5	4.45	0 50 71	475 635 700	310	5.8	Same sample as in test no. 75, but reduced before use for 16 hrs at 600°F with H_2
77 (8/27)	3-G	Ni Metal Powder	9.5	4.45	0 50 81	380 560 670	310	5.8	Nickel metal powder (approx. 200 mesh) was prepared from Nickel oxide by reduction with H_2 for 16 hours at 600°F.
78 (8/27)	3-G	Pt on 1/8" Al_2O_3 Kies. (10 cc)	9.5	4.45	0 40	375 590	310	5.8	0.5% Palladium on 1/8" alumina pellets was reduced for two hrs at 500°F with H_2
79 (8/28)	3-G	Co(G-61) 1/8"x3/16" Kies. (10 cc)	9.5	4.45	0 43 79 81 87 97	300 355 420 450 475 675	310	5.8	Girdler Catalyst No. G-61, Cobalt on Kieselguhr, was reduced for 16 hrs with H_2 at 325°F.
80 (8/31)	3-G	Cb_2O_5 Powder (7 cc)	9.5	4.45	0	650	450	9.8	Columbium pentoxide was prepared by oxidation of Columbium metal with oxygen at 800°F. No pretreatment with hydrogen. Up to 15% carbon monoxide formed at 600-650°F. Pentoxide changed in color from white to grey, possibly a different oxide of columbium.

Test No.	Reactor No.	Catalyst	CO_2 Feed cc/min	$H_2:CO_2$	% CO_2 conv.	Catalyst Temp. °F	Space[a] Vel. Hr^{-1}	Stay Time Sec.	Remarks
81 (9/1)	3-G	0.5% Os on 1/8" Al_2O_3 Pellets (10 cc)	9.15	4.45	0 71 78	400 645 660	310	5.8	Catalyst reduced 16 hrs at 375°F in H_2.
82 (9/4)	3-G	Ta_2C_5 powder (10 cc)	9.15	4.45	0	600	310	5.8	Catalyst not reduced prior to use.
83 (9/8)	3-G	Ni powder (10 cc)	9.15	4.45	0 0 24 52 92 99	375 405 430 455 475 500	310	5.8	Prepared by decomposition of reagent grade nickel formate
84 (9/9)	3-G	W powder (10 cc)	9.15	4.45	0	650	310	5.8	Reduced for two hours at 650°F.
85 (9/9)	3-G	Mo powder (10 cc)	9.15	4.45	0 12	300 630	310	5.8	Reduced 16 hours at 400°F in H_2
86 (9/10)	3-G	Co powder (10 cc)	9.15	4.45	0 65	445 650	310	5.8	Reduced 70 min. at 625°F in H_2
87 (9/11)	3-G	Cb powder (10 cc)	9.15	4.45	0 30	300 660	310	5.8	Fine mesh (150-200) reduced 36 hours at 350°F.
88 (9/12)	3-G	Ni-T 311 (10 cc)	9.15	4.45	0 17	460 650	310	5.8	Catalyst not reduced prior to use. Ni0 on activated Al_2O_3 1/8" pellets.
89 (9/14)	3-G	Ni on multicel (10 cc)	9.15	4.45	91 86	530 675	310	5.8	Prepared from nickel formate precipated on multicel and decomposed at 500°F.
90 (9/14)	3-G	Ni on multicel (10 cc)	9.15	4.45	52 68 88 94	405 415 420 550	310	5.8	Prepared by dissolving $Ni(COOH)_2$ in conc. NH_4OH and adding multicel to form a thin paste. Paste was heated at 200°F to remove NH_3 and H_2O and then decomposed at 500°F.
91 (9/15)	3-G	Ni on multicel (10 cc)	9.15	4.45	23 75 97 100	365 415 460 520	310	5.8	Catalyst same as in run of 9/14. Reduced 16 hrs at 530°F in H_2
92 (9/16)	3-G	Mo-1201 (10 cc)	9.15	4.45	0	600	310	5.8	MoO_3 on Al_2O_3 pellets not reduced prior to use.
93 (9/17)	3-G	5 Pt on carbon black (10 cc)	9.15	4.45	32 44 47.5	450 515 625	310	5.8	catalyst reduced 16 hrs at 500°F.
94 (9/18)	3-G	Pt on Filtercel (10 cc)	9.15	4.45	0 35	550 630	310	5.8	Prepared by precipitating Pt on Filtercel in a slurry with sodium formate. Pt ~25% wt. of catalyst.
95 (9/29)	3-G	Ru on 1/8" Al_2O_3 spheres	9.15	4.45	0 12.5 41.5 49.0 52	475 550 635 675 705	310	5.8	Prepared by condensing RuO_4 vapor on surface of high surface area 1/8" Al_2O_3 spheres. No reduction prior to use.
96 (9/30)	3-G	Ru on 1/8" Al_2O_3 spheres	9.15	4.45	3 26.5 46.5	550 635 705	310	5.8	Catalyst of test #95 reduced overnight at 300°F in H_2.
97 (10/1)	3-G	Ru on 1/8" Al_2O_3 spheres	9.15	4.45	0 26.5	550 635	310	5.8	Prepared by immersing spheres in RuO_4-H_2O solution followed by evaporating to dryness. Reduced overnight at 300°F.
98 (10/1)	3-G	Ru on 1/8" Al_2O_3 spheres	9.15	4.45	0 17	635 695	310	5.8	Prepared by immersing spheres in perchloric acid-RuO_2 mixture.
99 (10/5)	3-G	0.5% Os on 1/8" Al_2O_3 Pellets (10 cc)	9.15	4.45	0	700	310	11.6	Catalyst washed with concentrated HNO_3 for 10 min. at room temperature.
100 (10/12)	3-G	5% Pd on Al_2O_3 Powder (10 cc)	9.15	4.45	0 55	400 625	310	11.6	Catalyst unreduced prior to use; obtained from Engelhard.

Test No.	Reactor No.	Catalyst	CO_2 Feed cc/min	$H_2:CO_2$	% CO_2 conv.	Catalyst Temp. °F	Space Vel. Hr^{-1} [a]	Stay Time Sec.	Remarks
101 (10/13)	3-G	5% Rh on Carbon Powder (10 cc)	9.15	4.45	0	650	310	11.6	Catalyst unreduced prior to use; obtained from Engelhard.
102 (10/14)	3-G	5% Rh on Carbon Powder (10 cc)	9.15	4.45	0	625	310	11.6	Same catalyst as 10/13, reduced 16 hours at 375°F.
103 (10/14)	3-G	5% Pd on Carbon Powder (10 cc)	9.15	4.45	0 37	375 550	310	11.6	Catalyst unreduced prior to use; obtained from Engelhard.
104 (10/15)	3-G	5% Pd on Carbon Powder (10 cc)	9.15	4.45	0 37	450 625	310	11.6	Same catalyst as 10/14, reduced 16 hours at 300°F.
105 (10/15)	3-G	Ni-0302	9.15	4.45	37	725	310	11.6	Catalyst obtained from Harshaw, reduced for 16 hrs at 400°F.
106 (10/19)	3-G	Ru on 1/8" Al_2O_3 Pellets	9.15	4.45	33 47	615 725	310	11.6	Catalyst prepared by vapor deposition of RuO_2 on bare alumina support, from RuO_4-H_2O solution.
107 (10/20)	3-G	Ru on 1/8" Al_2O_3 Pellets	9.15	4.45	0	600	310	11.6	Pellets vapor-deposited with RuO_2, from RuO_4-H_2O solution followed by oxidation in pure O_2 at 900°F, followed by reduction in H_2O for 16 hrs at 250°F.
108 (10/28)	3-G	Ru on 200-mesh stainless-steel gauze	9.15	4.45	0	600	310	11.6	The catalyst was prepared by immersing 200-mesh stainless-steel gauze which is in direct contact with pure nickel foil, in a RuO_4-H_2O solution. The gauze was then cut into circles the same radius as the 3-G reactor and mounted on a stainless steel thermowell.
109 (10/29)	3-G	Ru on 200 mesh Nickel gauze	9.15	4.45	0	725	310	11.6	This catalyst was prepared in the same fashion as the stainless-steel gauze catalyst mentioned in Test #108, with the exceptions that nickel gauze alone was placed in the RuO_4 solution; and the plated gauze was cut into thin strips and wound into small balls.

Test No.	Reactor No.	Catalyst	CO_2 Feed cc/min	$H_2:CO_2$	% CO_2 conv.	Catalyst Temp. °F	Space Vel. Hr^{-1}	Stay Time Sec.	Remarks
110 (11/2)	3-G	0.5% Ru on Al_2O_3 10 cc	9.15	4.45	1 60 83	475 555 675	310	12	1/8" pellets (Engelhard) were ground to 200-mesh powder and tested without prior reduction
111 (11/3)	3-G	2:1 mixture of 0.5% Ru on Al_2O_3, 0.5% Pt on Al_2O_3 (10 cc)	9.15	4.45	1 77	410 610	310	12	1/8" pellets (Engelhard) were ground to 200-mesh powder. Then 10 cc 0.5% Ru on Al_2O_3 was thoroughly mixed with 5 cc 0.5% Pt on Al_2O_3. This mixture of powders was then reduced for two hrs at 200°F in hydrogen, and subsequently tested.
112 (11/4)	3-G	2:1 mixture of 0.5% Ru on Al_2O_3, 0.5% Pt on Al_2O_3 (10 cc)	9.15	4.45	1 71 84	465 600 690	310	12	Same mixture as Test #111, but in addition, mixture was reduced for 16 hours at 210°F and then tested.
113 (11/5)	3-G	1:1 mixture of 0.5% Ru on Al_2O_3, 0.5% Pd on Al_2O_3 (10 cc)	9.15	4.45	1 61 95	420 465 700	310	12	1/8" pellets (Engelhard) were ground to 200-mesh powder. Then 5 cc 0.5% Ru on Al_2O_3 was thoroughly mixed with 5 cc 0.5% Pd on Al_2O_3, and subsequently tested.
114 (11/6)	3-G	Catalyst of Test #113 (10 cc)	9.15	4.45	0 98	400 650	310	12	Catalyst of Test #113 reduced 16 hrs at 100°F in H_2-CO_2 ambient.
115 (11/10)	3-G	0.5% Pd on Al_2O_3	9.15	4.45	1 71 90	500 700 750	310	12	1/8" pellets (Englehard) were ground to 200-mesh powder and subsequently tested.
116 (11/18)	3-G	Ru metal powder (10 cc)	9.15	4.45	35 100	385 435			This powder was a combination of powders obtained from Engelhard and Goldsmith. The powder was boiled in 5N HNO_3 for 10 min. and then thoroughly washed prior to use.
117 (11/20)	3-G	Ru metal powder (10 cc)	9.15	4.45	1 32 47 67 99	350 400 410 420 435	310	12	Same powder tested in Test #116.
118 (11/23)	3-G	Ru metal powder (10 cc)	9.15	4.45	98	440	310	12	Same catalyst as the one tested in test #117. The reactor was held under a vacuum during this run, the pressure in reactor being 10 psia.
119 (11/24)	3-G	Ru metal powder (10 cc)	9.15	4.45	72 98	400 450	310	12	Same catalyst is in test #118. The reactor was again held under a vacuum, the pressure being 5 psia.
120 (11/25)	3-G	Ni-0104 powder (10 cc)	9.15	4.45	93	485	310	12	Same catalyst as tested in test #47. Reduced for 16 hrs at 315°F prior to use. Reactor held under vacuum, the pressure being 3 psia.
121 (11/25)	3-G	Ni-0104 powder (10 cc)	9.15	4.45	97	485	310	12	Same catalyst as in test #120. Reactor under vacuum, pressure being 10 psia.
122 (11/25)	3-G	Ni-0104 powder (10 cc)	9.15	4.45	97	485	310	12	Same catalyst as in Test #121. Reactor under atmospheric pressure.
123 (11/25 to 12/24)	3-G	Ru metal powder (10 cc)	9.15	4.45	98	435	310	12	Same catalyst as in Tests #[illegible] 19. Reactor at atmospheric pressure. Duration run for thirty days did not change performance or appearance of catalyst. Conversion varied between 98 and 99%. Hydrogen sulfide injected into feed gas stream at 15 min. intervals, quantity 0.01 cc., for periods of six hours on 27th to 29th days did not cause any change in conversion.

APPENDIX C

CATALYST LISTING

CATALYST LISTING

Catalyst	Manufacturer	Mfr. No.	Support[a]	FORM			Sample No.	Test No.
				1/8" Pel.	150-250 Mesh	Other		
Ruthenium	Engelhard	-----	Pure Metal		X		---	46-2,48,53,54
"	Goldsmith	-----	Pure Metal		X		---	46-1
"	MRD	-----	Pure Metal		X		---	56
"	Engelhard, Goldsmith	-----	Pure Metal		X		54	116-119,123
"	Engelhard	-----	Alumina	X			33	1-15,20,21,24,31, 37,38,43,44
"	Engelhard	-----	Alumina		X		51 57,66	22,23,45,62,110
"	MRD	-----	Alumina	X			59	106,107
"	MRD	-----	Alumina			1/8" Spheres	45	95-98
"	MRD	-----	000 Milticel	X			53	51
"	MRD	-----	000 Milticel		X		62	52,60
"	Engelhard	-----	Carbon		X		71,72	64
"	MRD	-----	St. Steel			200-Mesh Gauze	63	108
"	MRD	-----	Nickel			200-Mesh Gauze	46	109
Ruthenium & Platinum	Engelhard	-----	Alumina		X	Originally 1/8" Pellets ground to 200-mesh pwdr	55	111,112
Ruthenium & Palladium	Engelhard	-----	Alumina		X	Originally 1/8" Pellets ground to 200-mesh pwdr	43	113,114
Rhodium	Engelhard	-----	Pure Metal		X		69	50,67
"	"	-----	Alumina	X			---	18
"	"	-----	Alumina		X		70	71
"	"	-----	Carbon		X		73-76	101,102
Iridium	Engelhard	-----	Pure Metal		X		65	74
"	"	-----	Alumina	X			24-32	16,17,68,72
Osmium	Engelhard	-----	Pure Metal		X		66	49
"	"	-----	Alumina	X			15-23	81,99
Platinum	Engelhard	-----	Carbon		X		77	93
"	MRD	-----	Filtercel		X		44	94
Palladium	Engelhard	-----	Alumina	X			9-14	78
"	"	-----	Alumina		X		58	100
"	"	-----	Carbon		X		79	103,104
"	"	-----	Alumina		X	Originally 1/8" Pellets	78	115
Nickel	MRD	-----	Pure Metal		X	From Nickel Formate	40	55,58,75,76,83
					X	From Nickel Oxide	---	77
"	Harshaw	Ni-0707	Alumina	X			3	39,40
"	Harshaw	Ni-0104	Kieselguhr	X			4	19,32,35,65
"	Harshaw	Ni-0104	Kieselguhr		X	Originally 1/8" Pellets	52	47,100,122
"	MRD	-----	000 Milticel		X	From Nickel Carbonate	61	61
"	MRD	-----	000 Milticel		X	From Nickel Formate	57	89-91
"	Girdler	T-326	Special			1/8" x 3/16" Pellets	6	66
"	Harshaw	Ni-0302	Alumina	X			1	105
Nickel Oxide	Girdler	T-311	Alumina	X			5	88
Nickel Amine	Girdler	T-325	Special	X			7	69,70
Cobalt	Harshaw	Co-0108	Kieselguhr	X			2	41,42,63
"	Girdler	G-61	Kieselguhr			1/8" x 3/16" Pellets	8	79
"	City Chem.	-----	Pure Metal		X		39	86
Columbium	Fansteel	-----	Pure Metal			80-200-Mesh Powder	41,42	73,87
Co_2O_5	MRD	-----	Pure Powder		X		50	80
Ta_2O_5	A.D. Mackay	-----	Pure Powder		X		36	82
Tungsten	"	-----	Pure Metal		X		64	84
Molybdenum	Fansteel	-----	Pure Metal		X		37,38	85

[a] All supported platinum group metals are 0.5% metal on 1/8" alumina pellets, and 5.0% metal on alumina or carbon powders.

UNCLASSIFIED
Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)
General American Transportation Corporation
MRD Division
Niles 48, Illinois

2a. REPORT SECURITY CLASSIFICATION
Unclassified

2b GROUP
N/A

3. REPORT TITLE

"Catalytic Reduction of Carbon Dioxide to Methane and Water"

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)
Final Report

5. AUTHOR(S) (Last name, first name, initial)

Remus, G. A.

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
April 1965	84	103

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
AF 33(615)1210	AFFDL-TR-65-12
b. PROJECT NO. 6146	
c. Task No. 614612	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
d.	MRD 1249-2030

10. AVAILABILITY/LIMITATION NOTICES

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	Air Force Flight Dynamics Laboratory

13. ABSTRACT A literature search was conducted to determine suitable candidate catalysts for the Sabtier reaction. A test system was designed and fabricated for evaluating the candidate catalysts material to select an optimum catalyst. The system included a reactor sized to handle 2.5 lbs of CO_2 per day, equivalent to one-man output. Three smaller reactors were also used to test more accurately the effects of changes in temperature, flow and catalyst configuration.

The optimum catalyst was determined to be ruthenium metal powder, having a bulk density of 85 lb/ft^3, and an average particle diameter of .002-.003 inches. The minimum temperature required with this catalyst to provide over 99% conversion of CO_2 was 357°F., at one atmosphere, a $H_2:CO_2$ ratio of 4.4 and a space velocity of 310 hr^{-1}. During a thirty-day duration test with ruthenium metal powder CO_2 conversion remained essentially at 99%, and the catalyst remained unchanged. A short period of intermittent injection of H_2S gas into the feed gas line did not affect performance. Operation at reduced pressures down to 5 psia caused only a 1-2% decrease in CO_2 conversion with all other parameters held constant.

The theoretical equilibrium reaction limitations are discussed in the report. Various laboratory catalyst preparations and their effects on the reaction are described, and conclusion and recommendations are listed at the end of the report.

DD FORM 1 JAN 64 1473

UNCLASSIFIED
Security Classification

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT

INSTRUCTIONS

1. ORIGINATING ACTIVITY: Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization *(corporate author)* issuing the report.

2a. REPORT SECURITY CLASSIFICATION: Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.

2b. GROUP: Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.

3. REPORT TITLE: Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.

4. DESCRIPTIVE NOTES: If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.

5. AUTHOR(S): Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.

6. REPORT DATE: Enter the date of the report as day, month, year; or month, year. If more than one date appears on the report, use date of publication.

7a. TOTAL NUMBER OF PAGES: The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7b. NUMBER OF REFERENCES: Enter the total number of references cited in the report.

8a. CONTRACT OR GRANT NUMBER: If appropriate, enter the applicable number of the contract or grant under which the report was written.

8b, 8c, & 8d. PROJECT NUMBER: Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.

9a. ORIGINATOR'S REPORT NUMBER(S): Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

9b. OTHER REPORT NUMBER(S): If the report has been assigned any other report numbers *(either by the originator or by the sponsor)*, also enter this number(s).

10. AVAILABILITY/LIMITATION NOTICES: Enter any limitations on further dissemination of the report, other than those imposed by security classification, using standard statements such as:

(1) "Qualified requesters may obtain copies of this report from DDC."

(2) "Foreign announcement and dissemination of this report by DDC is not authorized."

(3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through _____."

(4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through _____."

(5) "All distribution of this report is controlled. Qualified DDC users shall request through _____."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. SUPPLEMENTARY NOTES: Use for additional explanatory notes.

12. SPONSORING MILITARY ACTIVITY: Enter the name of the departmental project office or laboratory sponsoring *(paying for)* the research and development. Include address.

13 ABSTRACT: Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as *(TS), (S), (C), or (U)*.

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14 KEY WORDS: Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, rules, and weights is optional.